Reports of the Finnish Environment Institute 41 | 2021

Interlaboratory Proficiency Test 04/2021

# Leaching behavior test: Up-flow percolation test

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## Abstract

**Interlaboratory Proficiency Test 04/2021**
Proftest SYKE carried out the proficiency test (PT) in cooperation with the KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste samples in spring 2021. The results of the up-flow percolation test (EN 14405:2017) for samples of bottom ash from biofuel combustion were compared and evaluated. In total, there were 7 participants in the PT. For all the measurands which were evaluated, the median or the mean of the reported results was used as the assigned value. The overall performance of the participants was evaluated by using $E_n$ scores and 72 % of the evaluated results were satisfactory. The participant results were also evaluated by means of D% scores and 51 % of those were ≤ |25 %|. The pH results were evaluated by means of z scores and 82 % of results were satisfactory. Warm thanks to all participants in this proficiency test!



**Keywords**: leaching test, up-flow percolation, waste landfill acceptance criteria, environmental laboratories, proficiency test, interlaboratory comparison



## Tiivistelmä

**Laboratorioiden välinen pätevyyskoe 04/2021**
Proftest SYKE järjesti yhteistyössä KVVY Tutkimus Oy:n kanssa keväällä 2021 pätevyyskokeen laboratorioille, jotka tekevät liukoisuustestejä jätteiden kaatopaikkakelpoisuuden arvioimiseksi. Pätevyyskokeessa vertailun kohteena oli läpivirtaustesti (EN 14405:2017) biopolttoaineen pohjatuhkalle. Pätevyyskokeeseen osallistui 7 laboratoriota. Arvioiduille testisuureille käytettiin vertailuarvona osallistujatulosten mediaania tai keskiarvoa. Pätevyyden arviointi tehtiin tässä vertailussa koko aineistolle $E_n$-arvojen avulla ja tuloksista oli hyväksyttäviä 72 %. Osallistujatuloksia arvioitiin myös D%-arvojen avulla ja 51 % niistä oli ≤ |25 %|. pH-määritysten tulokset arvioitiin z-arvoilla ja 82 % tuloksista oli hyväksyttäviä. Kiitos pätevyyskokeen osallistujille!



**Asiasanat**: liukoisuustesti, läpivirtaustesti, kaatopaikkakelpoisuus, ympäristölaboratoriot, pätevyyskoe, laboratorioiden välinen vertailumittaus



## Sammandrag

**Provningsjämförelse 04/2021**
Proftest SYKE genomförde i samarbete med förening KVVY Tutkimus Oy en provningsjämförelse under våren 2021 för laktester som används vid bedömningen av avfall som ska deponeras på deponi. Resultaten av uppströms perkolationstest (EN 14405:2017) för bottenaska av biobränslen jämfördes och värderades. Tillsammans 7 laboratorier deltog i jämförelse. För de analyter som var utvärderade användes antingen det medelvärdet eller median av deltagarnas resultat som referensvärde av analytens koncentration. Alla resultaten värderades med hjälp av $E_n$-värden och 72 % av resultaten var acceptabla. Resultaten värderades också med D%-värden och 51 % av dessa var ≤ |25 %|. Resultaten för pH enhet värderades med z-värden och 82 % var acceptabla. Ett varmt tack till alla deltagarna i testet!



**Nyckelord**: laktest, uppström perkolationstest, klassificering av avfall för deponi, miljölaboratorier, provningsjämförelse,

# Contents

# 1 Introduction

Proftest SYKE carried out the proficiency test (PT) in cooperation with the KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste sample in spring 2021 (LT 04/2021). In this proficiency test, the results of the up-flow percolation test (EN 14405:2017) for samples of bottom ash from biofuel combustion were compared and evaluated [1]. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), $Cl^-$, $SO_4^{2-}$, $F^-$, DOC, pH, and conductivity.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [2] and applying ISO 13528 [3] and IUPAC Technical report [4]. Proftest SYKE is accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). The organizing of this proficiency test is included in the accreditation scope of Proftest SYKE.

# 2 Organizing the proficiency test

## 2.1 Responsibilities

**Organizer**

Proftest SYKE, Finnish Environment Institute SYKE, Laboratory Centre
Mustialankatu 3, FI-00790 Helsinki, Finland
Phone: +358 295 251 000, Email: *proftest@syke.fi*

**The responsibilities in organizing the proficiency test**

| | |
|---|---|
| Riitta Koivikko | coordinator |
| Mirja Leivuori | substitute for coordinator |
| Keijo Tervonen | technical assistance |
| Markku Ilmakunnas | technical assistance |
| Sari Lanteri | technical assistance |
| Ritva Väisänen | technical assistance |

**Cooperation partner and expert laboratory**

KVVY Tutkimus Oy (T064, www.finas.fi/sites/en)

| | | |
|---|---|---|
| **Analytical experts** | Up-flow percolation test | Marika Kaasalainen (KVVY) |
| | Metals | Timo Sara-Aho (SYKE) |
| | pH and conductivity | Raija Ivalo (KVVY) |
| | Anions (IC) | Suvi Pöyhönen (KVVY) |
| | DOC | Tea Niemistö (KVVY) |

| | |
|---|---|
| **Subcontracting** | KVVY: Sample material preparation, homogenization and dividing into subsamples, leaching test (pretest, homogeneity) and the needed chemical and physico-chemical analysis. |

## 2.2 Participants

Nine laboratories registered to participate in this PT, but two of them informed that they do not report their results. Thus, the final number of participants in this proficiency test was 7, three of them from Finland and four from abroad (Appendix 1). Altogether 71 % of the participants used accredited analytical methods at least for a part of the measurements. For this PT, the expert laboratory has code 2 in the result tables.

## 2.3 Samples and delivery

The sample LT1 delivered to the participants was bottom ash from biofuel combustion collected from Finland, sample size was about 600 g. This waste is included in the scope of the Government Decree 843/2017 [5]. The sample material was sieved to 1 mm particle size before homogenization and dividing into sub samples.

The samples were delivered to the participants abroad on 22 and to national participants on 23 March 2021. The samples arrived to the participants at the latest on 25 March 2021.

The up-flow percolation test (EN 14405:2017) was to be conducted at the latest by 28 May 2021. The measurands (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Z), $Cl^-$, $SO_4^{2-}$, $F^-$, DOC, pH, and conductivity) were to be determined from the test fractions 1–7. Also, cumulative values L/S 2 and L/S 10 were to be calculated. If the result in one or more eluate fraction was below the limit of detection, the cumulative values were to be reported with upper and lower limit values (according to EN 14405:2017). For measurands that had no below the limit of detection result in fractions, the results were to be reported to L/S 2, lower and L/S 10, lower. The concentrations of the measurands were to be expressed as the leached amounts (mg/kg dry weight) relative to the total mass of the sample. The used sample codes in the results tables were:

**F1 = Sample LT1, Fraction 1**
**F2 = Sample LT1, Fraction 2**
**F3 = Sample LT1, Fraction 3**
**F4 = Sample LT1, Fraction 4**
**F5 = Sample LT1, Fraction 5**
**F6 = Sample LT1, Fraction 6**
**F7 = Sample LT1, Fraction 7**
**LS_2lower = Sample LT1, L/S 2, lower limit result**
**LS_2upper = Sample LT1, L/S 2, upper limit result**
**LS10lower = Sample LT1, L/S 10, lower limit result**
**LS10upper = Sample LT1, L/S 10, upper limit result**

All participants reported the results at the latest on 8 June 2021 as requested. The preliminary results report was delivered to the participants via ProftestWEB and email on 18 June 2021.

## 2.4 Sample pretesting and homogeneity

The material suitability for up-flow percolation test was tested by conducting the up-flow percolation test and analyzing all the measurands prior dividing the material into subsamples.

The homogeneity of the samples was tested by conducting one stage batch leaching test for 3 samples and by analyzing the measurands: Ba, Cr, Cu, Pb, Mo, $Cl^-$, $F^-$, $SO_4$, DOC, pH, and conductivity (Appendix 2). According to the homogeneity test results, the samples were considered homogenous.

## 2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 3. The comments from the participants dealt e.g. with the calculations of the cumulative values for L/S 2 and L/S 10. The comments from the provider were related e.g. to the reported measurement uncertainties. All the feedback from the proficiency test is valuable and is exploited when improving the activities.

## 2.6 Processing the data

### 2.6.1 Pretesting the data

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs test before calculating the mean. The results which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling. If the result has been reported as below detection limit, it has not been included in the statistical calculations. More information about the statistical handling of the data is available from the Guide for participant [6].

### 2.6.2 Assigned values

Detailed information of the assigned values, their uncertainties and reliability is shown in Appendix 4.

The leachability for some measurands was low and for many participants close or below the limit of detection/quantification. Further, the number of reported results was in many cases low. Thus, the assigned value was not set for following measurands in the following fractions as well as their cumulative values (where applicable):

- As: F5-F7, L/S 2 (upper limit), L/S 10 (upper limit)
- Cd: F1-F7, L/S 2 (lower and upper limit), L/S 10 (lower and upper limit)
- $Cl^-$: L/S 10 (upper limit)
- Cr: F5-F7, L/S 2 (upper limit), L/S 10 (upper limit)
- Cu: L/S 2 (upper limit), L/S 10 (upper limit)
- DOC: L/S 2 (lower limit)
- $F^-$: F6-F7, L/S 2 (upper limit), L/S 10 (upper limit)
- Hg: F1-F7, L/S 2 (lower and upper limit), L/S 10 (lower and upper limit)
- Mo: L/S 2 (upper limit)
- Ni: F1-F7, L/S 2 (lower and upper limit), L/S 10 (lower and upper limit)
- Pb: L/S 2 (upper limit), L/S 10 (upper limit)
- Sb: F5-F7, L/S 2 (lower and upper limit), L/S 10 (lower and upper limit)
- Se: F5-F7, L/S 2 (upper limit), L/S 10 (upper limit)
- $SO_4$: L/S 10 (upper limit)
- V: F5-F7, L/S 2 (upper limit), L/S 10 (upper limit)

For all the measurands, which were evaluated, the median or the mean of the results reported by the participants was used as the assigned value. The assigned values based on the median or the mean are not metrologically traceable values. As it was not possible to have metrologically traceable assigned values, the best available values were selected to be used as the assigned values. The reliability of the assigned values for pH results was statistically tested [3, 4].

When the median or the mean of the results reported by the participants was used as the assigned value, the uncertainty was calculated using the standard deviation of the reported results [3]. When the standard deviation of the reported results was high the expanded uncertainty of the assigned value was not calculated.

The expanded uncertainty of the assigned values varied between 1.1 % and 79.6 % (at the 95 % confidence level, Appendix 4). **After reporting the preliminary result report no changes have been done for the assigned values.**

### 2.6.3 Proficiency assessment procedure

In this proficiency test, the number of reported results was low and, thus, the overall performance evaluation was done by means of $E_n$ scores. They are given when the assigned value and the expanded uncertainty of the assigned value were set. Further, the $E_n$ scores were calculated when participant had reported the expanded measurement uncertainty with their result.

As the expanded measurement uncertainty was reported only by some participants, the participant results were evaluated also by means of D% scores. Those give the difference between the assigned value and reported participant results. D% can be interpreted as the measurement error for the results, to the extent to which the assigned value can be considered reference quantity value. The D% scores were given to all measurands and samples for which the assigned value was set.

The results for pH were evaluated by means of z scores. The standard deviation for proficiency assessment was estimated based on the uncertainty of the assigned value, the results of homogeneity test, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment ($2\times s_{pt}$, at the 95 % confidence level) was set to 0.5 pH units. **After reporting the preliminary result report no changes have been done for the standard deviations of the proficiency assessment values.**

When evaluating the results by means of z scores and using the median or the mean as the assigned value, the reliability of the assigned value was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where $u_{pt}$ is the standard uncertainty of the assigned value and $s_{pt}$ is the standard deviation for proficiency assessment [3, 4]. Further, the reliability of the standard deviation for proficiency assessment ($s_{pt}$) and the corresponding z score was estimated by comparing $s_{pt}$ with the standard deviation (s) of the reported results (the uniformity criterion $s_{rob}$ (or s) / $s_{pt} \leq 1.2$) [4].

*Only pH results were evaluated based on z scores and almost in each case the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this proficiency test. The uniformity criterion was met in each case.*

# 3 Results and conclusions

## 3.1 Results

The summary of the results of the PT is presented in Table 1. The terms in the results table are explained in Appendix 5. The results and the performance of each participant are presented in Appendix 6. The summaries of the $E_n$, D% and z scores are shown in Appendices 7, 8 and 9 and z scores in the ascending order in Appendix 10.

Table 1. The summary of the results in the proficiency test LT 04/2021.

| Measurand | Sample | Unit | Assigned value | Mean | Median | s | s % | 2 x $s_{pt}$ % | $n_{all}$ | Acc $E_n$ % / Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|
| As | F1 | mg/kg | 0.074 | 0.074 | 0.074 | 0.035 | 47.2 | - | 6 | 75 / - |
| | F2 | mg/kg | 0.050 | 0.047 | 0.050 | 0.015 | 32.1 | - | 5 | 67 / - |
| | F3 | mg/kg | 0.051 | 0.055 | 0.051 | 0.031 | 57.5 | - | 5 | 67 / - |
| | F4 | mg/kg | 0.0097 | 0.0097 | 0.0059 | 0.0097 | 99.8 | - | 5 | - / - |
| | F5 | mg/kg | - | 0.0001 | 0.0001 | 0.0001 | 141.4 | - | 5 | - / - |
| | F6 | mg/kg | - | 0.0005 | 0.0005 | 0.0006 | 141.4 | - | 5 | - / - |
| | F7 | mg/kg | - | 0.0006 | 0.0006 | 0.0008 | 141.4 | - | 5 | - / - |
| | LS_2lower | mg/kg | 0.19 | 0.19 | 0.20 | 0.07 | 34.7 | - | 4 | 50 / - |
| | LS_2upper | mg/kg | - | 0.27 | 0.27 | 0.03 | 12.7 | - | 3 | - / - |
| | LS10lower | mg/kg | 0.19 | 0.19 | 0.20 | 0.07 | 34.7 | - | 4 | 50 / - |
| | LS10upper | mg/kg | - | 0.33 | 0.33 | 0.10 | 30.5 | - | 4 | - / - |
| Ba | F1 | mg/kg | 0.20 | 0.21 | 0.20 | 0.11 | 54.2 | - | 6 | 100 / - |
| | F2 | mg/kg | 0.17 | 0.19 | 0.17 | 0.13 | 67.2 | - | 5 | - / - |
| | F3 | mg/kg | 0.83 | 0.91 | 0.83 | 0.22 | 24.7 | - | 5 | 67 / - |
| | F4 | mg/kg | 1.27 | 1.84 | 1.27 | 1.12 | 60.8 | - | 5 | 67 / - |
| | F5 | mg/kg | 37.3 | 49.0 | 37.3 | 38.9 | 79.4 | - | 5 | - / - |
| | F6 | mg/kg | 209 | 220 | 209 | 77 | 35.2 | - | 5 | 67 / - |
| | F7 | mg/kg | 208 | 212 | 208 | 18 | 8.6 | - | 5 | 100 / - |
| | LS_2lower | mg/kg | 40.0 | 53.4 | 40.0 | 43.3 | 81.1 | - | 4 | - / - |
| | LS10lower | mg/kg | 496 | 496 | 468 | 88 | 17.7 | - | 5 | 33 / - |
| Cd | F1 | mg/kg | - | 0.0003 | 0.0004 | 0.0001 | 42.7 | - | 6 | - / - |
| | F2 | mg/kg | - | 0.0005 | 0.0002 | 0.0005 | 98.9 | - | 5 | - / - |
| | F3 | mg/kg | - | 0.0006 | 0.0004 | 0.0005 | 86.8 | - | 5 | - / - |
| | F4 | mg/kg | - | 0.0005 | 0.0005 | 0.0000 | 0.0 | - | 5 | - / - |
| | LS_2lower | mg/kg | - | 0.0051 | 0.0004 | 0.0086 | 167.3 | - | 4 | - / - |
| | LS_2upper | mg/kg | - | 0.042 | 0.023 | 0.051 | 121.8 | - | 3 | - / - |
| | LS10lower | mg/kg | - | 0.0051 | 0.0004 | 0.0086 | 167.2 | - | 4 | - / - |
| | LS10upper | mg/kg | - | 0.066 | 0.054 | 0.069 | 105.4 | - | 4 | - / - |
| Cl | F1 | mg/kg | 756 | 675 | 756 | 298 | 44.1 | - | 6 | 50 / - |
| | F2 | mg/kg | 414 | 382 | 414 | 71 | 18.7 | - | 5 | 67 / - |
| | F3 | mg/kg | 207 | 227 | 207 | 93 | 40.9 | - | 5 | 33 / - |
| | F4 | mg/kg | 72.7 | 72.7 | 51.0 | 40.7 | 56.0 | - | 5 | 0 / - |
| | F5 | mg/kg | 11.7 | 11.7 | 10.0 | 3.3 | 28.3 | - | 5 | 67 / - |
| | F6 | mg/kg | 24.4 | 24.4 | 22.5 | 5.0 | 20.3 | - | 5 | 100 / - |
| | F7 | mg/kg | 26.7 | 26.7 | 23.6 | 9.5 | 35.6 | - | 5 | 100 / - |
| | LS_2lower | mg/kg | 1512 | 1512 | 1552 | 192 | 12.7 | - | 4 | 50 / - |
| | LS10lower | mg/kg | 1606 | 1573 | 1606 | 163 | 10.4 | - | 5 | 67 / - |

Table 1. The summary of the results in the proficiency test LT 04/2021.

| Measurand | Sample | Unit | Assigned value | Mean | Median | s | s % | 2 x $s_{pt}$ % | $n_{all}$ | Acc $E_n$ % / Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|
| Conductivity | F1 | mS/m | 33265 | 32950 | 33265 | 2642 | 8.0 | - | 6 | 100 / - |
| | F2 | mS/m | 34800 | 33653 | 34800 | 3251 | 9.7 | - | 5 | 50 / - |
| | F3 | mS/m | 32600 | 32498 | 32600 | 3053 | 9.4 | - | 5 | 100 / - |
| | F4 | mS/m | 15600 | 16582 | 15600 | 5073 | 30.6 | - | 5 | 50 / - |
| | F5 | mS/m | 1970 | 1912 | 1970 | 796 | 41.7 | - | 5 | 50 / - |
| | F6 | mS/m | 1122 | 1119 | 1122 | 46 | 4.1 | - | 5 | 100 / - |
| | F7 | mS/m | 753 | 753 | 966 | 410 | 54.5 | - | 6 | 67 / - |
| Cr | F1 | mg/kg | 0.41 | 0.43 | 0.41 | 0.20 | 47.6 | - | 6 | 50 / - |
| | F2 | mg/kg | 0.17 | 0.19 | 0.17 | 0.09 | 50.6 | - | 5 | 33 / - |
| | F3 | mg/kg | 0.26 | 0.24 | 0.26 | 0.06 | 26.9 | - | 5 | 67 / - |
| | F4 | mg/kg | 0.075 | 0.075 | 0.091 | 0.045 | 60.8 | - | 5 | 33 / - |
| | F5 | mg/kg | - | 0.0007 | 0.0007 | 0.0003 | 42.3 | - | 5 | - / - |
| | F6 | mg/kg | - | 0.0006 | 0.0006 | 0.0006 | 94.3 | - | 5 | - / - |
| | LS_2lower | mg/kg | 0.84 | 0.88 | 0.84 | 0.42 | 47.7 | - | 4 | 50 / - |
| | LS10lower | mg/kg | 1.08 | 1.35 | 1.08 | 1.00 | 74.2 | - | 5 | 33 / - |
| Cu | F1 | mg/kg | 0.11 | 0.13 | 0.11 | 0.07 | 54.7 | - | 6 | 100 / - |
| | F2 | mg/kg | 0.088 | 0.092 | 0.088 | 0.041 | 44.4 | - | 5 | 33 / - |
| | F3 | mg/kg | 0.11 | 0.13 | 0.11 | 0.08 | 61.6 | - | 5 | 67 / - |
| | F4 | mg/kg | 0.042 | 0.048 | 0.042 | 0.031 | 65.8 | - | 5 | 50 / - |
| | F5 | mg/kg | 0.0082 | 0.0082 | 0.0093 | 0.0068 | 82.1 | - | 5 | - / - |
| | F6 | mg/kg | 0.032 | 0.032 | 0.046 | 0.026 | 81.4 | - | 5 | - / - |
| | F7 | mg/kg | 0.033 | 0.033 | 0.043 | 0.027 | 82.7 | - | 5 | - / - |
| | LS_2lower | mg/kg | 0.26 | 0.28 | 0.26 | 0.12 | 43.9 | - | 4 | 50 / - |
| | LS_2upper | mg/kg | - | 3.59 | 3.59 | 4.56 | 127.2 | - | 2 | - / - |
| | LS10lower | mg/kg | 0.23 | 0.28 | 0.23 | 0.15 | 53.0 | - | 5 | 67 / - |
| | LS10upper | mg/kg | - | 3.68 | 3.68 | 4.55 | 123.7 | - | 2 | - / - |
| DOC | F1 | mg/kg | 420 | 475 | 420 | 375 | 78.9 | - | 4 | - / - |
| | F2 | mg/kg | 396 | 396 | 480 | 200 | 50.5 | - | 3 | 100 / - |
| | F3 | mg/kg | 926 | 926 | 1003 | 557 | 60.2 | - | 3 | 100 / - |
| | F4 | mg/kg | 279 | 279 | 297 | 211 | 75.9 | - | 3 | - / - |
| | F5 | mg/kg | 18.8 | 18.8 | 22.9 | 8.1 | 42.9 | - | 3 | 100 / - |
| | F6 | mg/kg | 41.0 | 41.0 | 43.0 | 24.4 | 59.6 | - | 3 | 100 / - |
| | F7 | mg/kg | 62.0 | 62.0 | 57.0 | 33.3 | 53.7 | - | 3 | 100 / - |
| | LS_2lower | mg/kg | - | 5964 | 5964 | 3995 | 67.0 | - | 2 | - / - |
| | LS10lower | mg/kg | 4309 | 4309 | 3187 | 4355 | 101.1 | - | 3 | - / - |
| F | F1 | mg/kg | 3.92 | 6.09 | 3.92 | 6.90 | 113.2 | - | 5 | - / - |
| | F2 | mg/kg | 6.04 | 6.04 | 6.41 | 4.16 | 69.0 | - | 4 | 100 / - |
| | F3 | mg/kg | 7.25 | 7.73 | 7.25 | 5.89 | 76.2 | - | 4 | - / - |
| | F4 | mg/kg | 2.58 | 2.63 | 2.58 | 1.54 | 58.3 | - | 4 | 33 / - |
| | F5 | mg/kg | 0.58 | 0.58 | 0.58 | 0.51 | 87.9 | - | 4 | - / - |
| | LS_2lower | mg/kg | 5.45 | 5.45 | 5.45 | 0.18 | 3.4 | - | 3 | - / - |
| | LS_2upper | mg/kg | - | 9.96 | 9.96 | 2.32 | 23.3 | - | 2 | - / - |
| | LS10lower | mg/kg | 7.96 | 7.96 | 6.90 | 3.05 | 38.3 | - | 4 | 67 / - |
| | LS10upper | mg/kg | - | 12.8 | 12.8 | 4.0 | 31.6 | - | 2 | - / - |

Table 1. The summary of the results in the proficiency test LT 04/2021.

| Measurand | Sample | Unit | Assigned value | Mean | Median | s | s % | 2 x $s_{pt}$ % | $n_{all}$ | Acc $E_n$ % / Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|
| Hg | F1 | mg/kg | - | 0.0017 | 0.0001 | 0.0028 | 168.4 | - | 6 | - / - |
| | F2 | mg/kg | - | 0.0018 | 0.0001 | 0.0031 | 170.3 | - | 5 | - / - |
| | F3 | mg/kg | - | 0.0028 | 0.0001 | 0.0048 | 169.3 | - | 5 | - / - |
| | F4 | mg/kg | - | 0.0010 | 0.0000 | 0.0018 | 170.6 | - | 5 | - / - |
| | LS_2lower | mg/kg | - | 0.093 | 0.000 | 0.161 | 173.2 | - | 3 | - / - |
| | LS_2upper | mg/kg | - | 0.15 | 0.15 | 0.18 | 118.2 | - | 3 | - / - |
| | LS10lower | mg/kg | - | 0.093 | 0.000 | 0.161 | 173.2 | - | 3 | - / - |
| | LS10upper | mg/kg | - | 0.17 | 0.17 | 0.18 | 111.5 | - | 4 | - / - |
| Mo | F1 | mg/kg | 0.33 | 0.30 | 0.33 | 0.11 | 38.6 | - | 6 | 50 / - |
| | F2 | mg/kg | 0.23 | 0.25 | 0.23 | 0.03 | 13.7 | - | 5 | 100 / - |
| | F3 | mg/kg | 0.28 | 0.28 | 0.28 | 0.03 | 10.6 | - | 5 | 67 / - |
| | F4 | mg/kg | 0.099 | 0.099 | 0.093 | 0.044 | 44.7 | - | 5 | 67 / - |
| | F5 | mg/kg | 0.0031 | 0.0031 | 0.0034 | 0.0020 | 63.5 | - | 5 | - / - |
| | F6 | mg/kg | 0.0031 | 0.0031 | 0.0031 | 0.0001 | 4.6 | - | 5 | - / - |
| | F7 | mg/kg | 0.0040 | 0.0040 | 0.0040 | 0.0000 | 0.0 | - | 5 | - / - |
| | LS_2lower | mg/kg | 1.01 | 1.01 | 1.01 | 0.06 | 5.4 | - | 4 | 50 / - |
| | LS_2upper | mg/kg | - | 6.28 | 6.28 | 7.30 | 116.2 | - | 2 | - / - |
| | LS10lower | mg/kg | 0.99 | 1.00 | 0.99 | 0.05 | 5.0 | - | 5 | 67 / - |
| | LS10upper | mg/kg | 1.22 | 4.59 | 1.22 | 6.01 | 130.9 | - | 3 | - / - |
| Ni | F1 | mg/kg | - | 0.0018 | 0.0022 | 0.0007 | 38.5 | - | 6 | - / - |
| | F2 | mg/kg | - | 0.0008 | 0.0011 | 0.0007 | 87.5 | - | 5 | - / - |
| | F3 | mg/kg | - | 0.0009 | 0.0010 | 0.0001 | 12.4 | - | 5 | - / - |
| | F4 | mg/kg | - | 0.0002 | 0.0002 | 0.0002 | 141.4 | - | 5 | - / - |
| | F5 | mg/kg | - | 0.0001 | 0.0001 | 0.0001 | 141.4 | - | 5 | - / - |
| | F6 | mg/kg | - | 0.0002 | 0.0002 | 0.0002 | 141.4 | - | 5 | - / - |
| | F7 | mg/kg | - | 0.001 | 0.001 | 0.000 | 0.0 | - | 5 | - / - |
| | LS_2lower | mg/kg | - | 0.0019 | 0.0015 | 0.0022 | 120.0 | - | 4 | - / - |
| | LS_2upper | mg/kg | - | 0.10 | 0.05 | 0.13 | 128.7 | - | 3 | - / - |
| | LS10lower | mg/kg | - | 0.001 | 0.000 | 0.002 | 173.2 | - | 4 | - / - |
| | LS10upper | mg/kg | - | 0.18 | 0.13 | 0.16 | 88.8 | - | 3 | - / - |
| Pb | F1 | mg/kg | 0.096 | 0.099 | 0.096 | 0.030 | 30.7 | - | 6 | 75 / - |
| | F2 | mg/kg | 0.080 | 0.080 | 0.077 | 0.015 | 18.9 | - | 5 | 100 / - |
| | F3 | mg/kg | 0.14 | 0.14 | 0.14 | 0.02 | 15.1 | - | 5 | 100 / - |
| | F4 | mg/kg | 0.082 | 0.082 | 0.084 | 0.012 | 14.9 | - | 5 | 100 / - |
| | F5 | mg/kg | 0.0095 | 0.0090 | 0.0095 | 0.0035 | 38.7 | - | 5 | 100 / - |
| | F6 | mg/kg | 0.016 | 0.016 | 0.016 | 0.003 | 19.1 | - | 5 | 100 / - |
| | F7 | mg/kg | 0.024 | 0.024 | 0.024 | 0.008 | 33.8 | - | 5 | 100 / - |
| | LS_2lower | mg/kg | 0.39 | 0.39 | 0.39 | 0.01 | 3.5 | - | 4 | 50 / - |
| | LS_2upper | mg/kg | - | 0.42 | 0.42 | 0.00 | 0.0 | - | 1 | - / - |
| | LS10lower | mg/kg | 0.43 | 0.42 | 0.43 | 0.03 | 7.5 | - | 5 | 67 / - |
| | LS10upper | mg/kg | - | 2.32 | 2.32 | 2.54 | 109.5 | - | 2 | - / - |
| pH | F1 | | 13.6 | 13.6 | 13.7 | 0.3 | 1.9 | 3.6 | 7 | 100 / 71 |
| | F2 | | 13.7 | 13.7 | 13.6 | 0.2 | 1.4 | 3.6 | 6 | 100 / 67 |
| | F3 | | 13.8 | 13.8 | 13.8 | 0.2 | 1.3 | 3.6 | 6 | 50 / 67 |
| | F4 | | 13.3 | 13.2 | 13.3 | 0.2 | 1.5 | 3.8 | 6 | 100 / 67 |

Table 1. The summary of the results in the proficiency test LT 04/2021.

| Measurand | Sample | Unit | Assigned value | Mean | Median | s | s % | 2 x $s_{pt}$ % | $n_{all}$ | Acc $E_n$ % / Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|
| pH | F5 | | 12.8 | 12.8 | 12.8 | 0.2 | 1.4 | 3.9 | 6 | 100 / 100 |
| | F6 | | 12.7 | 12.6 | 12.7 | 0.3 | 2.1 | 3.9 | 6 | 100 / 100 |
| | F7 | | 12.7 | 12.7 | 12.8 | 0.3 | 2.1 | 3.9 | 7 | 100 / 100 |
| Sb | F1 | mg/kg | 0.0035 | 0.0035 | 0.0020 | 0.0026 | 75.8 | - | 6 | - / - |
| | F2 | mg/kg | 0.0019 | 0.0019 | 0.0020 | 0.0005 | 24.1 | - | 5 | 100 / - |
| | F3 | mg/kg | 0.0087 | 0.0087 | 0.0030 | 0.0106 | 121.7 | - | 5 | - / - |
| | F4 | mg/kg | 0.0031 | 0.0031 | 0.0010 | 0.0036 | 117.3 | - | 5 | - / - |
| | F5 | mg/kg | - | 0.0021 | 0.0021 | 0.0030 | 141.4 | - | 5 | - / - |
| | F6 | mg/kg | - | 0.0046 | 0.0046 | 0.0065 | 141.4 | - | 5 | - / - |
| | F7 | mg/kg | - | 0.0055 | 0.0055 | 0.0078 | 141.4 | - | 5 | - / - |
| | LS_2lower | mg/kg | - | 0.0034 | 0.0033 | 0.0039 | 115.6 | - | 4 | - / - |
| | LS_2upper | mg/kg | - | 0.068 | 0.048 | 0.074 | 108.1 | - | 3 | - / - |
| | LS10lower | mg/kg | - | 0.0023 | 0.0000 | 0.0040 | 173.2 | - | 4 | - / - |
| | LS10upper | mg/kg | - | 0.17 | 0.17 | 0.06 | 34.8 | - | 3 | - / - |
| Se | F1 | mg/kg | 0.049 | 0.049 | 0.050 | 0.022 | 44.5 | - | 6 | 67 / - |
| | F2 | mg/kg | 0.025 | 0.025 | 0.025 | 0.006 | 25.0 | - | 5 | 100 / - |
| | F3 | mg/kg | 0.032 | 0.032 | 0.025 | 0.017 | 53.7 | - | 5 | 100 / - |
| | F4 | mg/kg | 0.0047 | 0.0066 | 0.0047 | 0.0060 | 91.5 | - | 5 | - / - |
| | F5 | mg/kg | - | 0.0001 | 0.0001 | 0.0001 | 141.4 | - | 5 | - / - |
| | F7 | mg/kg | - | 0.002 | 0.002 | 0.000 | 0.0 | - | 5 | - / - |
| | LS_2lower | mg/kg | 0.11 | 0.11 | 0.12 | 0.02 | 19.6 | - | 4 | 50 / - |
| | LS_2upper | mg/kg | - | 0.20 | 0.20 | 0.11 | 53.7 | - | 3 | - / - |
| | LS10lower | mg/kg | 0.11 | 0.11 | 0.12 | 0.02 | 18.5 | - | 4 | 50 / - |
| | LS10upper | mg/kg | - | 0.38 | 0.38 | 0.23 | 60.1 | - | 4 | - / - |
| $SO_4$ | F1 | mg/kg | 2350 | 2332 | 2350 | 660 | 28.3 | - | 6 | 75 / - |
| | F2 | mg/kg | 2300 | 2444 | 2300 | 565 | 23.1 | - | 5 | 100 / - |
| | F3 | mg/kg | 5990 | 5718 | 5990 | 895 | 15.6 | - | 5 | 100 / - |
| | F4 | mg/kg | 2813 | 2273 | 2813 | 1516 | 66.7 | - | 5 | - / - |
| | F5 | mg/kg | 6.96 | 8.93 | 6.96 | 6.99 | 78.3 | - | 5 | - / - |
| | F6 | mg/kg | 4.93 | 8.46 | 4.93 | 9.72 | 114.9 | - | 5 | - / - |
| | F7 | mg/kg | 7.31 | 7.31 | 8.50 | 2.06 | 28.2 | - | 5 | 100 / - |
| | LS_2lower | mg/kg | 13206 | 13206 | 14160 | 1691 | 12.8 | - | 4 | 50 / - |
| | LS10lower | mg/kg | 13290 | 13016 | 13290 | 1442 | 11.1 | - | 5 | 67 / - |
| | LS10upper | mg/kg | - | 14205 | 14205 | 660 | 28.3 | - | 1 | - / - |
| V | F1 | mg/kg | 0.13 | 0.12 | 0.13 | 0.05 | 38.3 | - | 5 | 67 / - |
| | F2 | mg/kg | 0.10 | 0.10 | 0.10 | 0.04 | 35.6 | - | 5 | 100 / - |
| | F3 | mg/kg | 0.11 | 0.11 | 0.11 | 0.03 | 30.6 | - | 5 | 67 / - |
| | F4 | mg/kg | 0.020 | 0.035 | 0.020 | 0.038 | 107.6 | - | 5 | - / - |
| | LS_2lower | mg/kg | 0.36 | 0.39 | 0.36 | 0.08 | 20.6 | - | 4 | 50 / - |
| | LS_2upper | mg/kg | - | 2.33 | 0.48 | 3.22 | 138.2 | - | 3 | - / - |
| | LS10lower | mg/kg | 0.36 | 0.39 | 0.36 | 0.08 | 20.6 | - | 4 | 50 / - |
| | LS10upper | mg/kg | - | 2.39 | 0.56 | 3.24 | 135.3 | - | 3 | - / - |
| Zn | F1 | mg/kg | 94.0 | 98.4 | 94.0 | 41.0 | 41.6 | - | 5 | 75 / - |
| | F2 | mg/kg | 79.8 | 78.2 | 79.8 | 22.5 | 28.7 | - | 4 | 67 / - |
| | F3 | mg/kg | 106 | 110 | 106 | 47 | 42.7 | - | 4 | 67 / - |
| | F4 | mg/kg | 31.7 | 33.8 | 31.7 | 23.8 | 70.4 | - | 4 | - / - |
| | F5 | mg/kg | 0.78 | 0.99 | 0.78 | 0.87 | 87.6 | - | 4 | - / - |

Table 1. The summary of the results in the proficiency test LT 04/2021.

| Measurand | Sample | Unit | Assigned value | Mean | Median | s | s % | 2 x $s_{pt}$ % | $n_{all}$ | Acc $E_n$ % / Acc z % |
|---|---|---|---|---|---|---|---|---|---|---|
| Zn | F6 | mg/kg | 0.66 | 0.73 | 0.66 | 0.44 | 59.9 | - | 4 | 67 / - |
| | F7 | mg/kg | 0.74 | 0.74 | 0.74 | 0.31 | 41.3 | - | 4 | 100 / - |
| | LS_2lower | mg/kg | 260 | 260 | 260 | 82 | 31.5 | - | 3 | - / - |
| | LS10lower | mg/kg | 278 | 278 | 312 | 65 | 23.5 | - | 4 | 67 / - |

s: the standard deviation, s %: the standard deviation as percent, $2\times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, $n_{all}$: the number of the participants, Acc. $E_n$ %: the results (%), where $|E_n| \leq 1.0$, Acc z %: the results (%), where $|z| \leq 2$.

## 3.2 Analytical procedures

The standard method EN 14405:2017 (up-flow percolation test) was used to determine the leaching properties of studied measurands from the bottom ash sample [1]. The sample material is subjected to percolation with water as a function of liquid to solid ratio under specified percolation conditions. The eluate is collected in separate fractions (from fraction 1 to fraction 7).

The details of the procedures the participants followed were collected via Webropol survey. Six participants replied to the survey (Appendix 11).

The participants were allowed to use different analytical methods for the measurements of the measurands' concentrations in the PT. The measurements of metals were mostly done by ICP-MS and for Hg either CV-AFS or ICP-MS was used. For $Cl^-$, $F^-$ and $SO_4$ measurements the participants mostly used EN ISO 10304 and for conductivity EN 27888. DOC was measured with EN 14848 (with two different approaches for filtered sample) and for pH both electrodes for low ionic water and waste water were used as well as the universal electrode. The statistical comparison of the analytical methods was not possible for the data due to low number of results ($n < 5$). Further, no signification differences were observed based on visual evaluation. CEN/TR 16192:2020 summarizes the analytical test methods for the waste eluates [7]. The used analytical test methods are listed in Appendix 12 and the reported results of the participants grouped by methods with their expanded uncertainties (k=2) are presented in Appendix 13.

The cumulatively released quantities L/S 2 and L/S 10 were to be calculated according to EN 14405:2017 [1].

> "*For each component the cumulatively released quantity shall be calculated by accumulating the released quantities of the specific component, measured in the different eluate fractions. Where the concentration of a component in one or more eluate fraction is below the lower detection limit, for this component two calculations shall be carried out, to indicate both the upper limit and the lower limit of the cumulatively released quantity.*
>
> *The upper limit of $U_i$ (the released quantity) shall be calculated by making $c_i$ (the concentration) equal to the limit of detection."*

The cumulatively released quantities reported by the participants are presented in Table 2 (see also Appendix 3, Feedback to the participants).

Table 2. Upper and lower limits for cumulatively released quantities L/S 2 and L/S 10 reported by participants.

| Measurand | Participant | Unit | LS_2lower | LS_2upper | LS10lower | LS10upper |
|---|---|---|---|---|---|---|
| As | 1 | mg/kg | 0.247 | 0.248 | 0.247 | 0.256 |
| | 2 | mg/kg | 0.197 | 0.297 | 0.197 | 0.397 |
| | 5 | mg/kg | 2.229 | 2.238 | 2.229 | 2.317 |
| | 6 | mg/kg | - | - | - | < 0.0619 |
| | 8 | mg/kg | 0.118 | - | 0.118 | - |
| Ba | 1 | mg/kg | 40.0 | - | 425 | - |
| | 2 | mg/kg | 18.4 | - | 468 | - |
| | 5 | mg/kg | 43.85 | - | 1189.48 | - |
| | 6 | mg/kg | - | - | 19.0 | - |
| | 8 | mg/kg | 101.91 | - | 593.85 | - |
| Cd | 1 | mg/kg | < 0.001 | - | < 0.005 | - |
| | 2 | mg/kg | 0 | 0.100 | 0 | 0.140 |
| | 5 | mg/kg | 0.015 | 0.023 | 0.015 | 0.054 |
| | 6 | mg/kg | - | - | - | < 0.00299 |
| | 8 | mg/kg | 0.00035 | 0.00305 | 0.00036 | 0.00306 |
| $Cl^-$ | 1 | mg/kg | 1552 | - | 1572 | 1597 |
| | 2 | mg/kg | 1680 | - | 1730 | - |
| | 5 | mg/kg | 17119.8 | - | 17223.2 | - |
| | 6 | mg/kg | - | - | 1640 | - |
| | 8 | mg/kg | 1302.5 | - | 1348.4 | - |
| Cr | 1 | mg/kg | 0.844 | - | 0.844 | 0.85 |
| | 2 | mg/kg | 1.31 | 1.36 | 1.31 | 1.46 |
| | 5 | mg/kg | 10.13 | 10.14 | 10.13 | 10.22 |
| | 6 | mg/kg | - | - | 2.76 | - |
| | 8 | mg/kg | 0.475 | - | 0.479 | - |
| Cu | 1 | mg/kg | 0.402 | - | 0.495 | - |
| | 2 | mg/kg | 0.261 | 0.361 | 0.261 | 0.461 |
| | 5 | mg/kg | 6.8 | 6.81 | 6.8 | 6.89 |
| | 6 | mg/kg | - | - | 0.199 | - |
| | 8 | mg/kg | 0.162 | - | 0.166 | - |
| DOC | 5 | mg/kg | 8788.58 | - | 9116.02 | - |
| | 6 | mg/kg | - | - | 625 | - |
| | 8 | mg/kg | 3139.5 | - | 3186.6 | - |
| $F^-$ | 2 | mg/kg | 5.58 | 11.6 | 5.58 | 15.6 |
| | 5 | mg/kg | 325.03 | - | 33.39 | - |
| | 6 | mg/kg | - | - | 11.4 | - |
| | 8 | mg/kg | 5.32 | 8.32 | 6.9 | 9.9 |
| Hg | 1 | mg/kg | - | < 0.0012 | - | < 0.003 |
| | 2 | mg/kg | 0 | 0.025 | 0 | 0.035 |
| | 5 | mg/kg | 0.278 | 0.28 | 0.278 | 0.296 |
| | 6 | mg/kg | - | - | - | <0.00199 |
| | 8 | mg/kg | 0 | - | 0 | - |
| Mo | 1 | mg/kg | - | - | 1.01 | 1.02 |
| | 2 | mg/kg | 1.07 | 1.12 | 1.07 | 1.22 |
| | 5 | mg/kg | 11.43 | 11.44 | 11.43 | 11.52 |
| | 6 | mg/kg | - | - | 0.962 | - |
| | 8 | mg/kg | 0.96 | - | 0.967 | - |
| Ni | 1 | mg/kg | 0.00449 | 0.00599 | < 0.01 | - |
| | 2 | mg/kg | 0 | 0.25 | 0 | 0.35 |
| | 5 | mg/kg | 0 | 0.048 | 0 | 0.127 |
| | 6 | mg/kg | - | - | - | 0.0498 |
| | 8 | mg/kg | 0.003 | - | 0.003 | - |

Table 2. Upper and lower limits for cumulatively released quantities L/S 2 and L/S 10 reported by participants.

| Measurand | Participant | Unit | LS_2lower | LS_2upper | LS10lower | LS10upper |
|---|---|---|---|---|---|---|
| Pb | 1 | mg/kg | 0.4 | - | 0.439 | - |
| | 2 | mg/kg | 0.373 | 0.423 | 0.373 | 0.523 |
| | 5 | mg/kg | 4.02 | - | 4.07 | 4.11 |
| | 6 | mg/kg | - | - | 0.427 | - |
| | 8 | mg/kg | 0.386 | - | 0.438 | - |
| Sb | 1 | mg/kg | 0.0066 | 0.0067 | < 0.01 | - |
| | 2 | mg/kg | 0 | 0.150 | 0 | 0.21 |
| | 5 | mg/kg | 0 | 0.048 | 0 | 0.127 |
| | 6 | mg/kg | - | - | - | < 0.0199 |
| | 8 | mg/kg | 0.007 | - | 0.007 | - |
| Se | 1 | mg/kg | 0.121 | 0.125 | 0.121 | 0.157 |
| | 2 | mg/kg | 0.128 | 0.278 | 0.128 | 0.378 |
| | 5 | mg/kg | 1.219 | 1.229 | 1.219 | 1.308 |
| | 6 | mg/kg | - | - | - | 0.619 |
| | 8 | mg/kg | 0.087 | - | 0.089 | - |
| $SO_4$ | 1 | mg/kg | 14160 | - | 14180 | 14205 |
| | 2 | mg/kg | 14204 | - | 14217 | - |
| | 5 | mg/kg | 117275.7 | - | 117286.8 | - |
| | 6 | mg/kg | - | - | 12400 | - |
| | 8 | mg/kg | 11253.4 | - | 11267 | - |
| V | 1 | mg/kg | 0.481 | 0.482 | 0.481 | 0.486 |
| | 2 | mg/kg | 0.361 | 0.461 | 0.361 | 0.561 |
| | 5 | mg/kg | 6.04 | 6.05 | 6.04 | 6.13 |
| | 8 | mg/kg | 0.328 | - | 0.328 | - |
| Zn | 2 | mg/kg | 318 | - | 320 | - |
| | 5 | mg/kg | 3741.11 | - | 3746 | - |
| | 6 | mg/kg | - | - | 312 | - |
| | 8 | mg/kg | 202.12 | - | 203 | - |

## 3.3 Uncertainties of the results

Altogether 57 % of the participants reported the expanded measurement uncertainties ($k$=2) with their results for at least some of their results (Appendices 13 and 14). The range of the reported uncertainties varied between the measurands and fractions (Table 3).

Table 3. The ranges of the expanded measurement uncertainties ($k$=2, U%) reported by the participants.

| Measurand | U% | Measurand | U% | Measurand | U% |
|---|---|---|---|---|---|
| **As** | 12.2 – 40 | **DOC** | 22 – 40 | **Sb** | 10.5 – 40 |
| **Ba** | 11.9 – 40 | **$F^-$** | 15 – 48 | **Se** | 22 – 40 |
| **Cd** | 11.6 – 40 | **Hg** | 22 – 40 | **$SO_4^{2-}$** | 10 – 40 |
| **$Cl^-$** | 10 – 40 | **Mo** | 14.5 – 40 | **V** | 16.3 – 40 |
| **Conductivity** | 10 – 22 | **Ni** | 14.9 – 40 | **Zn** | 12.4 – 40 |
| **Cr** | 13.6 – 40 | **Pb** | 15.3 – 40 | | |
| **Cu** | 13.1 – 40 | **pH** | 0.4 – 22 | | |

The most used approaches to estimate the measurement uncertainty were based on the internal quality control data and on the data from method validation (Appendix 14). One participant used MUkit measurement uncertainty software for the estimation of their uncertainties [8]. The free software is available on the webpage: www.syke.fi/envical/en [8, 9]. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

# 4 Evaluation of the results

The evaluation of the participants was based on the $E_n$, D%, and z scores. $E_n$ and z scores were interpreted as follows:

| Criteria | Performance |
|---|---|
| $-1.0 \leq E_n \leq 1.0$ | Satisfactory |
| $E_n < -1.0$ or $E_n > 1.0$ | Unsatisfactory |
| $\lvert z \rvert \leq 2$ | Satisfactory |
| $2 < \lvert z \rvert < 3$ | Questionable |
| $\lvert z \rvert \geq 3$ | Unsatisfactory |

In total, 72 % of the results evaluated by means of $E_n$ scores were satisfactory (Appendix 7). The participant results were evaluated also by means of D% scores and 51 % of the D% scores were ≤ |25 %| (Appendix 8). Only the pH results were evaluated by means of z scores and 82 % of those results were satisfactory when deviation of 0.5 pH unit from the assigned values was accepted (Appendix 9). The summary of the performance is presented in Table 4.

The share of satisfactory $E_n$ results for fractions F1-F7 was higher in this PT than in the previous similar PT LT 14/2017 [10]. For the cumulative values, the share of satisfactory $E_n$ scores was lower than in the previous similar PT.

Table 4. Summary of the performance evaluation in the proficiency test LT 04/2021.

| Sample | Measurand | $E_n$ scores, satisfactory results % | D% scores, range | z scores: 2 x $s_{pt}$%, Satisfactory results % | Remarks |
|---|---|---|---|---|---|
| LT1 F1-F7 | metals | 76 % | -94 % – 350 % | – | 23 % of the D% scores were ≤ \|25 %\|. |
| | anions | 71 % | -87 % – 5432 % | – | 45 % of the D% scores were ≤ \|25 %\|. |
| | conductivity | 74 % | -86 % – 522 % | – | $E_n$ scores were calculated mostly only for two participants. 58 % of the D% scores were ≤ \|25 %\|. |
| | pH | 93 % | -8.0 % – 6.3 % | 0.5 pH units, 82 % | 100 % of the D% scores were ≤ \|25 %\|. Also, in the PT LT 14/2017 the pH results were evaluated with z scores and 87 % of results were satisfactory [7]. |
| | DOC | 100 % | -79 % – 116 % | – | $E_n$ scores were calculated only for one participant. 22 % of the D% scores were ≤ \|25 %\|. |
| LT1 L/S 2, lower | metals | 50 % | -54 % – 2515 % | – | 51 % of the D% scores were ≤ \|25 %\|. |
| | anions | 50 % | -15 % – 5864 % | – | 73 % of the D% scores were ≤ \|25 %\|. |
| LT1 L/S 10, lower | metals | 54 % | -96 % – 2857 % | – | 56 % of the D% scores were ≤ \|25 %\|. |
| | anions | 67 % | -30 % – 4088 % | – | 64 % of the D% scores were ≤ \|25 %\|. |
| | DOC | – | -86 % – 112 % | – | - |

# 5 Summary

Proftest SYKE carried out the proficiency test (PT) in cooperation with the KVVY Tutkimus Oy for the laboratories conducting leaching tests for solid waste samples in spring 2021 (LT 04/2021). The results of the up-flow percolation test (EN 14405:2017) for samples of bottom ash from biofuel combustion were compared and evaluated. The tested measurands were metals (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn), $Cl^-$, $SO_4^{2-}$, $F^-$, DOC, pH, and conductivity. In total, there were 7 participants in this PT.

For all the measurands which were evaluated, the median or the mean of the reported results was used as the assigned value. The overall performance of the participants was evaluated by using $E_n$ scores and 72 % of the evaluated results were satisfactory. The participant results were also evaluated by means of D% scores and 51 % of those were ≤ |25 %|. The pH results were evaluated by means of z scores and 82 % of results were satisfactory.

# 6 Summary in Finnish

Proftest SYKE järjesti yhteistyössä KVVY Tutkimus Oy:n kanssa keväällä 2021 pätevyyskokeen laboratorioille, jotka tekevät liukoisuustestejä jätteiden kaatopaikkakelpoisuuden arvioimiseksi (LT 04/2021). Pätevyyskokeessa vertailun kohteena oli läpivirtaustesti (EN 14405:2017) biopolttoaineen pohjatuhkalle. Liukoisuustestin fraktioista analysoitiin metallit (As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, V, Zn) sekä testisuureet $Cl^-$, $SO_4^{2-}$, $F^-$, DOC, pH ja sähkönjohtavuus. Pätevyyskokeeseen osallistui 7 laboratoriota.

Arvioiduille testisuureille käytettiin vertailuarvona osallistujatulosten mediaania tai keskiarvoa. Pätevyyden arviointi tehtiin tässä vertailussa koko aineistolle $E_n$-arvojen avulla ja tuloksista oli hyväksyttäviä 72 %. Osallistujatuloksia arvioitiin myös D%-arvojen avulla ja 51 % niistä oli ≤ |25 %|. pH-määritysten tulokset arvioitiin z-arvoilla ja 82 % tuloksista oli hyväksyttäviä.

## References


1. EN 14405:2017 Characterization of waste. Leaching behavior test. Up-flow percolation test (under specified conditions).

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3. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.

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## Appendix 1. Participants in the proficiency test

| Country | Participant |
|---|---|
| **Czech Republic** | ALS Czech Republic s.r.o. |
| **Finland** | Eurofins Ahma Oy, Oulu |
| | Eurofins Labtium Oy, Kuopio |
| | KVVY Tutkimus Oy, Tampere |
| **Greece** | Athens Analysis Laboratories S.A. |
| **Sweden** | Eurofins Water Testing Sweden AB |
| | SYNLAB Analytics & Services Sweden AB |

## Appendix 2. Homogeneity of the samples

The homogeneity of the samples tested by conducting one stage batch leaching test for 3 samples and by analyzing the measurands: Ba, Cr, Cu, Pb, Mo, $Cl^-$, $F^-$, $SO_4$, DOC, pH, and conductivity.

**Criterion for homogeneity:**

$$s_{sam}/s_h < 0.5, \text{ where}$$

$s_{sam}$ = between-sample deviation, standard deviation of the results between sub samples
$s_h$ = standard deviation for homogeneity testing

| Measurand | Concentration [mg/kg] | n | $s_h$ % | $s_h$ | $s_{sam}$ | $s_{sam}$ / $s_h$ | $s_{sam}$ / $s_h$ < 0.5 ? |
|---|---|---|---|---|---|---|---|
| Ba | 8.13 | 3 | 15 | 1.22 | 0.503 | 0.413 | Yes |
| $Cl^-$ | 1567 | 3 | 15 | 235 | 115 | 0.491 | Yes |
| Conductivity | 4883 | 3 | 1 | 48.8 | 15.3 | 0.313 | Yes |
| Cr | 0.85 | 3 | 10 | 0.085 | 0.036 | 0.424 | Yes |
| Cu | 0.05 | 3 | 5 | 0.0027 | 0.0006 | 0.213 | Yes |
| DOC | 310 | 3 | 15 | 46.5 | 17.3 | 0.373 | Yes |
| $F^-$ | 5.87 | 3 | 10 | 0.587 | 0.153 | 0.260 | Yes |
| Mo | 0.85 | 3 | 5 | 0.043 | 0.015 | 0.358 | Yes |
| Pb | 0.39 | 3 | 10 | 0.039 | 0.015 | 0.395 | Yes |
| pH | 13 | 3 | 1 | 0.13 | 0.000 | 0000 | Yes |
| $SO_4^{2-}$ | 8367 | 3 | 15 | 1255 | 472 | 0.377 | Yes |

**Conclusion:** All criteria for homogeneity were fulfilled and the samples could be considered homogenous.

# Appendix 3. Feedback from the proficiency test

## Feedback from the participants

| Participant | Comments on technical excecution | Action / Proftest SYKE |
|---|---|---|
| 6 | The participant did two-step up-flow percolation test. One fraction at L/S 0.1 and the other fractions (2-7) as a collective sample as L/S 9.9. Therefore, the participant reported fraction 1 and L/S 10 for the PT. | The PT is according to the standard and the results evaluation is done accordingly. |
| | During the analysis there was an incident and some of the liquid leaked out. The participant calculated the lost amount and compensated that in the calculations for the collective sample. | Thank you for the information. Unfortunate situation in which the participant needs to estimate the status of their results. |
| | As the participant did not have all the fractions, it was not straightforward when to write on lower or upper limit. The participant made it like this: | The PT is according to the standard and the results evaluation is done accordingly. |
| | - If there was no value below limit of detection the results is written on "lower limit". | Correct. |
| | - If there was a value on fraction 1 and a value below limit of detection on L/S10 the results is written on "upper limit". | The PT is according to the standard and the results evaluation is done accordingly. |
| | - If there was below limit of detection on both fraction 1 and on L/S10 the result is written on "upper limit". | |
| | - When reporting the measurement uncertainty, the participant has only written the one for the leaching (22 %) and not for the analysis. | The reported measurement uncertainties are summarized in Table 3. |

| Participant | Comments to the results | Action / Proftest SYKE |
|---|---|---|
| 6 | The participant wondered the participants' practices how to calculate the upper and lower limits. | The provider thanks the participant for bringing up their observations. |
| | • Shouldn't the lower limit be 0 if all the fractions are < detection limit? | Below the limit of detection value should be calculated as 0 value to the cumulative lower limit. |
| | • How is it possible that a participant has reported all their fractions 1-7 with a value (no < limit of detection) but at the same time they have reported both a lower and upper limit with a value? | |

## Feedback to the participants

| Participant | Comments |
|---|---|
| 4 | The measurement uncertainty should be reported with the results obtained by accredited methods. |
| 5 | The calculations for cumulative values L/S 2 and L/S 10 do not correlate with the results from the fractions 1-7. Recalculations are recommended. |
| 8 | The participant reports some results as 0 mg/kg (e.g. As F5-F7). Such results should be reported as below limit of quantification, LOQ (e.g. < 0.0005 mg/kg). |
| All participants | Despite all participants were using the same standard method, the reported lower and upper limits vary between participants. Calculations are possibly not done in the same way.<br>It is important to continue to exploit the means of external quality assurance procedures in order to reach the mutual understanding of the requirements of the standard method. |

## Appendix 4. Evaluation of the assigned values and their uncertainties

| Measurand | Sample | Unit | Assigned value | $U_{pt}$ | $U_{pt}$, % | Evaluation method of assigned value | $u_{pt}/s_{pt}$ |
|---|---|---|---|---|---|---|---|
| As | F1 | mg/kg | 0.074 | 0.029 | 38.6 | Median | - |
| | F2 | mg/kg | 0.050 | 0.014 | 28.7 | Median | - |
| | F3 | mg/kg | 0.051 | 0.026 | 51.4 | Median | - |
| | F4 | mg/kg | 0.0097 | - | - | Mean | - |
| | LS_2lower | mg/kg | 0.19 | 0.08 | 40.1 | Mean | - |
| | LS10lower | mg/kg | 0.19 | 0.08 | 40.1 | Mean | - |
| Ba | F1 | mg/kg | 0.20 | 0.09 | 44.2 | Median | - |
| | F2 | mg/kg | 0.17 | - | - | Median | - |
| | F3 | mg/kg | 0.83 | 0.18 | 22.1 | Median | - |
| | F4 | mg/kg | 1.27 | 0.69 | 54.4 | Median | - |
| | F5 | mg/kg | 37.3 | - | - | Median | - |
| | F6 | mg/kg | 209 | 66 | 31.5 | Median | - |
| | F7 | mg/kg | 208 | 16 | 7.7 | Median | - |
| | LS_2lower | mg/kg | 40.0 | - | - | Median | - |
| | LS10lower | mg/kg | 496 | 101 | 20.4 | Mean | - |
| Cl | F1 | mg/kg | 756 | 272 | 36.0 | Median | - |
| | F2 | mg/kg | 414 | 69 | 16.7 | Median | - |
| | F3 | mg/kg | 207 | 85 | 40.9 | Median | - |
| | F4 | mg/kg | 72.7 | 36.4 | 50.1 | Mean | - |
| | F5 | mg/kg | 11.7 | 3.0 | 25.3 | Mean | - |
| | F6 | mg/kg | 24.4 | 4.4 | 18.2 | Mean | - |
| | F7 | mg/kg | 26.7 | 9.5 | 35.6 | Mean | - |
| | LS_2lower | mg/kg | 1512 | 222 | 14.7 | Mean | - |
| | LS10lower | mg/kg | 1606 | 167 | 10.4 | Median | - |
| Conductivity | F1 | mS/m | 33265 | 2661 | 8.0 | Median | - |
| | F2 | mS/m | 34800 | 3376 | 9.7 | Median | - |
| | F3 | mS/m | 32600 | 3064 | 9.4 | Median | - |
| | F4 | mS/m | 15600 | 4274 | 27.4 | Median | - |
| | F5 | mS/m | 1970 | 735 | 37.3 | Median | - |
| | F6 | mS/m | 1122 | 46 | 4.1 | Median | - |
| | F7 | mS/m | 753 | 367 | 48.7 | Mean | - |
| Cr | F1 | mg/kg | 0.41 | 0.16 | 38.9 | Median | - |
| | F2 | mg/kg | 0.17 | 0.08 | 45.2 | Median | - |
| | F3 | mg/kg | 0.26 | 0.06 | 24.0 | Median | - |
| | F4 | mg/kg | 0.075 | 0.041 | 54.4 | Mean | - |
| | LS_2lower | mg/kg | 0.84 | 0.46 | 55.1 | Median | - |
| | LS10lower | mg/kg | 1.08 | 0.80 | 74.2 | Median | - |
| Cu | F1 | mg/kg | 0.11 | 0.05 | 44.7 | Median | - |
| | F2 | mg/kg | 0.088 | 0.035 | 39.7 | Median | - |
| | F3 | mg/kg | 0.11 | 0.06 | 55.1 | Median | - |
| | F4 | mg/kg | 0.042 | 0.028 | 65.8 | Median | - |
| | F5 | mg/kg | 0.0082 | - | - | Mean | - |
| | F6 | mg/kg | 0.032 | - | - | Mean | - |
| | F7 | mg/kg | 0.033 | - | - | Mean | - |
| | LS_2lower | mg/kg | 0.26 | 0.13 | 50.6 | Median | - |
| | LS10lower | mg/kg | 0.23 | 0.12 | 53.0 | Median | - |

| Measurand | Sample | Unit | Assigned value | $U_{pt}$ | $U_{pt}$, % | Evaluation method of assigned value | $u_{pt}/s_{pt}$ |
|---|---|---|---|---|---|---|---|
| DOC | F1 | mg/kg | 420 | - | - | Median | - |
| | F2 | mg/kg | 396 | 231 | 58.3 | Mean | - |
| | F3 | mg/kg | 926 | 644 | 69.5 | Mean | - |
| | F4 | mg/kg | 279 | - | - | Mean | - |
| | F5 | mg/kg | 18.8 | 9.3 | 49.6 | Mean | - |
| | F6 | mg/kg | 41.0 | 28.2 | 68.8 | Mean | - |
| | F7 | mg/kg | 62.0 | 38.4 | 62.0 | Mean | - |
| | LS10lower | mg/kg | 4309 | - | - | Mean | - |
| F | F1 | mg/kg | 3.92 | - | - | Median | - |
| | F2 | mg/kg | 6.04 | 4.81 | 79.6 | Mean | - |
| | F3 | mg/kg | 7.25 | - | - | Median | - |
| | F4 | mg/kg | 2.58 | 1.50 | 58.3 | Median | - |
| | F5 | mg/kg | 0.58 | - | - | Mean | - |
| | LS_2lower | mg/kg | 5.45 | - | - | Median | - |
| | LS10lower | mg/kg | 7.96 | 3.53 | 44.3 | Mean | - |
| Mo | F1 | mg/kg | 0.33 | 0.10 | 31.5 | Median | - |
| | F2 | mg/kg | 0.23 | 0.03 | 12.2 | Median | - |
| | F3 | mg/kg | 0.28 | 0.03 | 10.6 | Median | - |
| | F4 | mg/kg | 0.099 | 0.040 | 40.0 | Mean | - |
| | F5 | mg/kg | 0.0031 | - | - | Mean | - |
| | F6 | mg/kg | 0.0031 | - | - | Mean | - |
| | F7 | mg/kg | 0.0040 | - | - | Mean | - |
| | LS_2lower | mg/kg | 1.01 | 0.06 | 6.3 | Mean | - |
| | LS10lower | mg/kg | 0.99 | 0.05 | 5.0 | Median | - |
| | LS10upper | mg/kg | 1.22 | - | - | Median | - |
| Pb | F1 | mg/kg | 0.096 | 0.024 | 25.0 | Median | - |
| | F2 | mg/kg | 0.080 | 0.014 | 17.0 | Mean | - |
| | F3 | mg/kg | 0.14 | 0.02 | 13.5 | Mean | - |
| | F4 | mg/kg | 0.082 | 0.011 | 13.4 | Mean | - |
| | F5 | mg/kg | 0.0095 | 0.0037 | 38.7 | Median | - |
| | F6 | mg/kg | 0.016 | 0.003 | 19.1 | Median | - |
| | F7 | mg/kg | 0.024 | 0.009 | 39.1 | Mean | - |
| | LS_2lower | mg/kg | 0.39 | 0.02 | 4.0 | Mean | - |
| | LS10lower | mg/kg | 0.43 | 0.03 | 7.5 | Median | - |
| pH | F1 | | 13.6 | 0.2 | 1.7 | Mean | 0.47 |
| | F2 | | 13.7 | 0.2 | 1.4 | Mean | 0.39 |
| | F3 | | 13.8 | 0.2 | 1.3 | Mean | 0.36 |
| | F4 | | 13.3 | 0.2 | 1.5 | Median | 0.39 |
| | F5 | | 12.8 | 0.1 | 1.1 | Median | 0.28 |
| | F6 | | 12.7 | 0.2 | 1.7 | Median | 0.44 |
| | F7 | | 12.7 | 0.2 | 1.6 | Mean | 0.41 |
| Sb | F1 | mg/kg | 0.0035 | - | - | Mean | - |
| | F2 | mg/kg | 0.0019 | 0.0005 | 27.9 | Mean | - |
| | F3 | mg/kg | 0.0087 | - | - | Mean | - |
| | F4 | mg/kg | 0.0031 | - | - | Mean | - |

| Measurand | Sample | Unit | Assigned value | $U_{pt}$ | $U_{pt}$, % | Evaluation method of assigned value | $u_{pt}/s_{pt}$ |
|---|---|---|---|---|---|---|---|
| Se | F1 | mg/kg | 0.049 | 0.020 | 39.8 | Mean | - |
| | F2 | mg/kg | 0.025 | 0.006 | 25.0 | Median | - |
| | F3 | mg/kg | 0.032 | 0.015 | 48.1 | Mean | - |
| | F4 | mg/kg | 0.0047 | - | - | Median | - |
| | LS_2lower | mg/kg | 0.11 | 0.02 | 22.6 | Mean | - |
| | LS10lower | mg/kg | 0.11 | 0.02 | 21.3 | Mean | - |
| $SO_4$ | F1 | mg/kg | 2350 | 543 | 23.1 | Median | - |
| | F2 | mg/kg | 2300 | 476 | 20.7 | Median | - |
| | F3 | mg/kg | 5990 | 839 | 14.0 | Median | - |
| | F4 | mg/kg | 2813 | - | - | Median | - |
| | F5 | mg/kg | 6.96 | - | - | Median | - |
| | F6 | mg/kg | 4.93 | - | - | Median | - |
| | F7 | mg/kg | 7.31 | 2.38 | 32.6 | Mean | - |
| | LS_2lower | mg/kg | 13206 | 1954 | 14.8 | Mean | - |
| | LS10lower | mg/kg | 13290 | 1475 | 11.1 | Median | - |
| V | F1 | mg/kg | 0.13 | 0.04 | 34.3 | Median | - |
| | F2 | mg/kg | 0.10 | 0.03 | 31.9 | Median | - |
| | F3 | mg/kg | 0.11 | 0.03 | 30.6 | Median | - |
| | F4 | mg/kg | 0.020 | - | - | Median | - |
| | LS_2lower | mg/kg | 0.36 | 0.09 | 23.8 | Median | - |
| | LS10lower | mg/kg | 0.36 | 0.09 | 23.8 | Median | - |
| Zn | F1 | mg/kg | 94.0 | 35.1 | 37.3 | Median | - |
| | F2 | mg/kg | 79.8 | 22.9 | 28.7 | Median | - |
| | F3 | mg/kg | 106 | 45 | 42.7 | Median | - |
| | F4 | mg/kg | 31.7 | - | - | Median | - |
| | F5 | mg/kg | 0.78 | - | - | Median | - |
| | F6 | mg/kg | 0.66 | 0.40 | 59.9 | Median | - |
| | F7 | mg/kg | 0.74 | 0.31 | 41.3 | Median | - |
| | LS_2lower | mg/kg | 260 | - | - | Mean | - |
| | LS10lower | mg/kg | 278 | 75 | 27.1 | Mean | - |

$U_{pt}$ = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
$s_{pt}$= the standard deviation for proficiency assessment
$u_{pt}$= the standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable.

## Appendix 5. Terms in the results tables

The information could be applied according to the PT.

**Measurand** The tested parameter

**Sample** The code of the sample

**Assigned value** The value attributed to a particular property of a proficiency test item

**Participant's result** The result reported by the participant (when replicate results are reported, the mean value)

**2 × $s_{pt}$ %** The standard deviation for proficiency assessment ($s_{pt}$) at the 95 % confidence level

**z score** Used for the participant's perfomance evaluation in the PT.
Calculated with formula:

$$z = (x_i - x_{pt})/s_{pt}, \text{ where}$$

$x_i$ = the result of the individual participant
$x_{pt}$ = the assigned value
$s_{pt}$ = the standard deviation for proficiency assessment

### Interpretation of the z scores

| | |
|---|---|
| $\lvert z \rvert \leq 2$ | Satisfactory |
| $2 < \lvert z \rvert < 3$ | Questionable (warning signal), the result deviates more than 2 × $s_{pt}$ from the assigned value. |
| $\lvert z \rvert \geq 3$ | Unsatisfactory (action signal), the result deviates more than 3 × $s_{pt}$ from the assigned value. |

**$E_n$ score** Error, normalized – Used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. Calculated with formula:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

$U_i$ = the expanded uncertainty of a participant's result
$U_{pt}$ = the expanded uncertainty of the assigned value

### Interpretation of the $E_n$ scores

| | |
|---|---|
| $\lvert E_n \rvert \leq 1.0$ | Satisfactory, should be taken as an indicator of successful performance when the uncertainties are valid. |
| $\lvert E_n \rvert > 1.0$ | Unsatisfactory (action signal), could indicate a need to review the uncertainty estimates, or to correct a measurement issue. |

**Md** Median

**s** Standard deviation

**s %** Standard deviation, %

**$n_{stat}$** Number of results in statistical processing

More information of the statistical calculations in international standards ISO/IEC 17043 and ISO 13528 as well as in Proftest SYKE Guide for participants [2, 3, 6].

## Appendix 6. Results of each participant

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| As | mg/kg | F1 | | | 0.074 | | 0.122 | 0.074 | 0.074 | 0.035 | 47.2 | 6 |
| | mg/kg | F2 | | | 0.050 | | 0.067 | 0.050 | 0.047 | 0.015 | 32.1 | 5 |
| | mg/kg | F3 | | | 0.051 | | 0.051 | 0.051 | 0.055 | 0.031 | 57.5 | 5 |
| | mg/kg | F4 | | | 0.0097 | | 0.0071 | 0.0059 | 0.0097 | 0.0097 | 99.8 | 4 |
| | mg/kg | F5 | | | | | *<0.001* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.003* | 0.0005 | 0.0005 | 0.0006 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | 0.0006 | 0.0006 | 0.0008 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | 0.19 | | 0.25 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS_2upper | | | | | 0.25 | 0.27 | 0.27 | 0.03 | 12.7 | 2 |
| | mg/kg | LS10lower | | | 0.19 | | 0.25 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS10upper | | | | | 0.26 | 0.33 | 0.33 | 0.10 | 30.5 | 2 |
| Ba | mg/kg | F1 | | | 0.20 | | 0.37 | 0.20 | 0.21 | 0.11 | 54.2 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.34 | 0.17 | 0.19 | 0.13 | 67.2 | 5 |
| | mg/kg | F3 | | | 0.83 | | 1.02 | 0.83 | 0.91 | 0.22 | 24.7 | 5 |
| | mg/kg | F4 | | | 1.27 | | 0.93 | 1.27 | 1.84 | 1.12 | 60.8 | 5 |
| | mg/kg | F5 | | | 37.3 | | 37.3 | 37.3 | 49.0 | 38.9 | 79.4 | 5 |
| | mg/kg | F6 | | | 209 | | 194 | 209 | 220 | 77 | 35.2 | 5 |
| | mg/kg | F7 | | | 208 | | 191 | 208 | 212 | 18 | 8.6 | 5 |
| | mg/kg | LS_2lower | | | 40.0 | | 40.0 | 40.0 | 53.4 | 43.3 | 81.1 | 3 |
| | mg/kg | LS10lower | | | 496 | | 425 | 468 | 496 | 88 | 17.7 | 3 |
| Cd | mg/kg | F1 | | | | | 0.0002 | 0.0004 | 0.0003 | 0.0001 | 42.7 | 3 |
| | mg/kg | F2 | | | | | 0.0002 | 0.0002 | 0.0005 | 0.0005 | 98.9 | 3 |
| | mg/kg | F3 | | | | | 0.0002 | 0.0004 | 0.0006 | 0.0005 | 86.8 | 3 |
| | mg/kg | F4 | | | | | *<0.00025* | 0.0005 | 0.0005 | 0.0000 | 0.0 | 1 |
| | mg/kg | F5 | | | | | *<0.0005* | | | | | |
| | mg/kg | F6 | | | | | *<0.0015* | | | | | |
| | mg/kg | F7 | | | | | *<0.0025* | | | | | |
| | mg/kg | LS_2lower | | | | | *<0.001* | 0.0004 | 0.0051 | 0.0086 | 167.3 | 3 |
| | mg/kg | LS10lower | | | | | *<0.005* | 0.0004 | 0.0051 | 0.0086 | 167.2 | 3 |
| Cl | mg/kg | F1 | | | 756 | | 868 | 756 | 675 | 298 | 44.1 | 6 |
| | mg/kg | F2 | | | 414 | | 414 | 414 | 382 | 71 | 18.7 | 5 |
| | mg/kg | F3 | | | 207 | | 213 | 207 | 227 | 93 | 40.9 | 4 |
| | mg/kg | F4 | | | 72.7 | | 48.0 | 51.0 | 72.7 | 40.7 | 56.0 | 5 |
| | mg/kg | F5 | | | 11.7 | | 9.3 | 10.0 | 11.7 | 3.3 | 28.3 | 5 |
| | mg/kg | F6 | | | 24.4 | | 19.0 | 22.5 | 24.4 | 5.0 | 20.3 | 5 |
| | mg/kg | F7 | | | 26.7 | | *<25* | 23.6 | 26.7 | 9.5 | 35.6 | 4 |
| | mg/kg | LS_2lower | | | 1512 | | 1552 | 1552 | 1512 | 192 | 12.7 | 3 |
| | mg/kg | LS10lower | | | 1606 | | 1572 | 1606 | 1573 | 163 | 10.4 | 4 |
| | mg/kg | LS10upper | | | | | 1597 | | | | | |
| Cr | mg/kg | F1 | | | 0.41 | | 0.29 | 0.41 | 0.43 | 0.20 | 47.6 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.18 | 0.17 | 0.19 | 0.09 | 50.6 | 5 |
| | mg/kg | F3 | | | 0.26 | | 0.29 | 0.26 | 0.24 | 0.06 | 26.9 | 5 |
| | mg/kg | F4 | | | 0.075 | | 0.091 | 0.091 | 0.075 | 0.045 | 60.8 | 5 |
| | mg/kg | F5 | | | | | 0.0007 | 0.0007 | 0.0007 | 0.0003 | 42.3 | 3 |
| | mg/kg | F6 | | | | | *<0.002* | 0.0006 | 0.0006 | 0.0006 | 94.3 | 2 |
| | mg/kg | F7 | | | | | *<0.004* | | | | | |

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Cr | mg/kg | LS_2lower | | | 0.84 | | 0.84 | 0.84 | 0.88 | 0.42 | 47.7 | 3 |
| | mg/kg | LS10lower | | | 1.08 | | 0.84 | 1.08 | 1.35 | 1.00 | 74.2 | 4 |
| | mg/kg | LS10upper | | | | | 0.85 | | | | | |
| Cu | mg/kg | F1 | | | 0.11 | | 0.15 | 0.11 | 0.13 | 0.07 | 54.7 | 6 |
| | mg/kg | F2 | | | 0.088 | | 0.088 | 0.088 | 0.092 | 0.041 | 44.4 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.11 | 0.11 | 0.13 | 0.08 | 61.6 | 5 |
| | mg/kg | F4 | | | 0.042 | | 0.049 | 0.042 | 0.048 | 0.031 | 65.8 | 4 |
| | mg/kg | F5 | | | 0.0082 | | 0.0093 | 0.0093 | 0.0082 | 0.0068 | 82.1 | 3 |
| | mg/kg | F6 | | | 0.032 | | 0.049 | 0.046 | 0.032 | 0.026 | 81.4 | 3 |
| | mg/kg | F7 | | | 0.033 | | 0.043 | 0.043 | 0.033 | 0.027 | 82.7 | 3 |
| | mg/kg | LS_2lower | | | 0.26 | | 0.40 | 0.26 | 0.28 | 0.12 | 43.9 | 3 |
| | mg/kg | LS10lower | | | 0.23 | | 0.50 | 0.23 | 0.28 | 0.15 | 53.0 | 4 |
| Hg | mg/kg | F1 | | | | | *<0.0004* | 0.0001 | 0.0017 | 0.0028 | 168.4 | 3 |
| | mg/kg | F2 | | | | | *<0.0004* | 0.0001 | 0.0018 | 0.0031 | 170.3 | 3 |
| | mg/kg | F3 | | | | | *<0.00006* | 0.0001 | 0.0028 | 0.0048 | 169.3 | 3 |
| | mg/kg | F4 | | | | | *<0.0001* | 0.0000 | 0.0010 | 0.0018 | 170.6 | 3 |
| | mg/kg | F5 | | | | | *<0.0002* | | | | | |
| | mg/kg | F6 | | | | | *<0.0006* | | | | | |
| | mg/kg | F7 | | | | | *<0.001* | | | | | |
| | mg/kg | LS_2upper | | | | | *<0.0012* | 0.15 | 0.15 | 0.18 | 118.2 | 2 |
| | mg/kg | LS10upper | | | | | *<0.003* | 0.17 | 0.17 | 0.18 | 111.5 | 2 |
| Mo | mg/kg | F1 | | | 0.33 | | 0.38 | 0.33 | 0.30 | 0.11 | 38.6 | 6 |
| | mg/kg | F2 | | | 0.23 | | 0.29 | 0.23 | 0.25 | 0.03 | 13.7 | 5 |
| | mg/kg | F3 | | | 0.28 | | 0.25 | 0.28 | 0.28 | 0.03 | 10.6 | 4 |
| | mg/kg | F4 | | | 0.099 | | 0.093 | 0.093 | 0.099 | 0.044 | 44.7 | 5 |
| | mg/kg | F5 | | | 0.0031 | | 0.0034 | 0.0034 | 0.0031 | 0.0020 | 63.5 | 3 |
| | mg/kg | F6 | | | 0.0031 | | *<0.003* | 0.0031 | 0.0031 | 0.0001 | 4.6 | 2 |
| | mg/kg | F7 | | | 0.0040 | | *<0.005* | 0.0040 | 0.0040 | 0.0000 | 0.0 | 2 |
| | mg/kg | LS_2lower | | | 1.01 | | 1.01 | 1.01 | 1.01 | 0.06 | 5.4 | 3 |
| | mg/kg | LS10lower | | | 0.99 | | 1.01 | 0.99 | 1.00 | 0.05 | 5.0 | 4 |
| | mg/kg | LS10upper | | | 1.22 | | 1.02 | 1.22 | 4.59 | 6.01 | 130.9 | 3 |
| Ni | mg/kg | F1 | | | | | 0.0022 | 0.0022 | 0.0018 | 0.0007 | 38.5 | 3 |
| | mg/kg | F2 | | | | | 0.0013 | 0.0011 | 0.0008 | 0.0007 | 87.5 | 3 |
| | mg/kg | F3 | | | | | 0.0010 | 0.0010 | 0.0009 | 0.0001 | 12.4 | 3 |
| | mg/kg | F4 | | | | | *<0.0005* | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F5 | | | | | *<0.001* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.003* | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | 0.001 | 0.001 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | | | 0.0045 | 0.0015 | 0.0019 | 0.0022 | 120.0 | 4 |
| | mg/kg | LS_2upper | | | | | 0.01 | 0.05 | 0.10 | 0.13 | 128.7 | 3 |
| | mg/kg | LS10lower | | | | | *<0.01* | 0.000 | 0.001 | 0.002 | 173.2 | 3 |
| Pb | mg/kg | F1 | | | 0.096 | | 0.081 | 0.096 | 0.099 | 0.030 | 30.7 | 6 |
| | mg/kg | F2 | | | 0.080 | | 0.077 | 0.077 | 0.080 | 0.015 | 18.9 | 5 |
| | mg/kg | F3 | | | 0.14 | | 0.16 | 0.14 | 0.14 | 0.02 | 15.1 | 5 |
| | mg/kg | F4 | | | 0.082 | | 0.081 | 0.084 | 0.082 | 0.012 | 14.9 | 5 |
| | mg/kg | F5 | | | 0.0095 | | 0.0046 | 0.0095 | 0.0090 | 0.0035 | 38.7 | 4 |
| | mg/kg | F6 | | | 0.016 | | 0.015 | 0.016 | 0.016 | 0.003 | 19.1 | 4 |
| | mg/kg | F7 | | | 0.024 | | 0.024 | 0.024 | 0.024 | 0.008 | 33.8 | 3 |

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Pb | mg/kg | LS_2lower | | | 0.39 | | 0.40 | 0.39 | 0.39 | 0.01 | 3.5 | 3 |
| | mg/kg | LS10lower | | | 0.43 | | 0.44 | 0.43 | 0.42 | 0.03 | 7.5 | 4 |
| pH | | F1 | | 0.41 | 13.6 | 3.6 | 13.7 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F2 | | -0.41 | 13.7 | 3.6 | 13.6 | 13.6 | 13.7 | 0.2 | 1.4 | 4 |
| | | F3 | | 0.00 | 13.8 | 3.6 | 13.8 | 13.8 | 13.8 | 0.2 | 1.3 | 4 |
| | | F4 | | 0.40 | 13.3 | 3.8 | 13.4 | 13.3 | 13.2 | 0.2 | 1.5 | 4 |
| | | F5 | | 0.00 | 12.8 | 3.9 | 12.8 | 12.8 | 12.8 | 0.2 | 1.4 | 6 |
| | | F6 | | 0.00 | 12.7 | 3.9 | 12.7 | 12.7 | 12.6 | 0.3 | 2.1 | 6 |
| | | F7 | | 0.40 | 12.7 | 3.9 | 12.8 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |
| Sb | mg/kg | F1 | | | 0.0035 | | 0.0019 | 0.0020 | 0.0035 | 0.0026 | 75.8 | 3 |
| | mg/kg | F2 | | | 0.0019 | | 0.0014 | 0.0020 | 0.0019 | 0.0005 | 24.1 | 3 |
| | mg/kg | F3 | | | 0.0087 | | 0.0022 | 0.0030 | 0.0087 | 0.0106 | 121.7 | 3 |
| | mg/kg | F4 | | | 0.0031 | | 0.0010 | 0.0010 | 0.0031 | 0.0036 | 117.3 | 3 |
| | mg/kg | F5 | | | | | *<0.001* | 0.0021 | 0.0021 | 0.0030 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.003* | 0.0046 | 0.0046 | 0.0065 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | 0.0055 | 0.0055 | 0.0078 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | | | 0.0066 | 0.0033 | 0.0034 | 0.0039 | 115.6 | 4 |
| | mg/kg | LS_2upper | | | | | 0.007 | 0.048 | 0.068 | 0.074 | 108.1 | 3 |
| | mg/kg | LS10lower | | | | | *<0.01* | 0.0000 | 0.0023 | 0.0040 | 173.2 | 3 |
| Se | mg/kg | F1 | | | 0.049 | | 0.058 | 0.050 | 0.049 | 0.022 | 44.5 | 5 |
| | mg/kg | F2 | | | 0.025 | | 0.031 | 0.025 | 0.025 | 0.006 | 25.0 | 4 |
| | mg/kg | F3 | | | 0.032 | | 0.025 | 0.025 | 0.032 | 0.017 | 53.7 | 5 |
| | mg/kg | F4 | | | 0.0047 | | 0.0069 | 0.0047 | 0.0066 | 0.0060 | 91.5 | 4 |
| | mg/kg | F5 | | | | | *<0.004* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.012* | | | | | |
| | mg/kg | F7 | | | | | *<0.02* | 0.002 | 0.002 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | 0.11 | | 0.12 | 0.12 | 0.11 | 0.02 | 19.6 | 3 |
| | mg/kg | LS_2upper | | | | | 0.13 | 0.20 | 0.20 | 0.11 | 53.7 | 2 |
| | mg/kg | LS10lower | | | 0.11 | | 0.12 | 0.12 | 0.11 | 0.02 | 18.5 | 3 |
| | mg/kg | LS10upper | | | | | 0.16 | 0.38 | 0.38 | 0.23 | 60.1 | 3 |
| $SO_4$ | mg/kg | F1 | | | 2350 | | 1670 | 2350 | 2332 | 660 | 28.3 | 6 |
| | mg/kg | F2 | | | 2300 | | 1670 | 2300 | 2444 | 565 | 23.1 | 5 |
| | mg/kg | F3 | | | 5990 | | 6830 | 5990 | 5718 | 895 | 15.6 | 5 |
| | mg/kg | F4 | | | 2813 | | 3960 | 2813 | 2273 | 1516 | 66.7 | 5 |
| | mg/kg | F5 | | | 6.96 | | 18.40 | 6.96 | 8.93 | 6.99 | 78.3 | 4 |
| | mg/kg | F6 | | | 4.93 | | 22.80 | 4.93 | 8.46 | 9.72 | 114.9 | 4 |
| | mg/kg | F7 | | | 7.31 | | *<25* | 8.50 | 7.31 | 2.06 | 28.2 | 3 |
| | mg/kg | LS_2lower | | | 13206 | | 14160 | 14160 | 13206 | 1691 | 12.8 | 3 |
| | mg/kg | LS10lower | | | 13290 | | 14180 | 13290 | 13016 | 1442 | 11.1 | 4 |
| | mg/kg | LS10upper | | | | | 14205 | 14205 | 14205 | 0 | 0.0 | 1 |
| V | mg/kg | F1 | | | 0.13 | | 0.17 | 0.13 | 0.12 | 0.05 | 38.3 | 5 |
| | mg/kg | F2 | | | 0.10 | | 0.13 | 0.10 | 0.10 | 0.04 | 35.6 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.15 | 0.11 | 0.11 | 0.03 | 30.6 | 4 |
| | mg/kg | F4 | | | 0.020 | | 0.029 | 0.020 | 0.035 | 0.038 | 107.6 | 4 |
| | mg/kg | F5 | | | | | *<0.0005* | | | | | |
| | mg/kg | F6 | | | | | *<0.0015* | | | | | |
| | mg/kg | F7 | | | | | *<0.0025* | | | | | |
| | mg/kg | LS_2lower | | | 0.36 | | 0.48 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |

| Participant 1 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| V | mg/kg | LS_2upper | | | | | 0.48 | 0.48 | 2.33 | 3.22 | 138.2 | 3 |
| | mg/kg | LS10lower | | | 0.36 | | 0.48 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| | mg/kg | LS10upper | | | | | 0.49 | 0.56 | 2.39 | 3.24 | 135.3 | 3 |

| Participant 2 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| As | mg/kg | F1 | | | 0.074 | | 0.092 | 0.074 | 0.074 | 0.035 | 47.2 | 6 |
| | mg/kg | F2 | | | 0.050 | | 0.052 | 0.050 | 0.047 | 0.015 | 32.1 | 5 |
| | mg/kg | F3 | | | 0.051 | | 0.053 | 0.051 | 0.055 | 0.031 | 57.5 | 5 |
| | mg/kg | F4 | | | 0.0097 | | *<0.05* | 0.0059 | 0.0097 | 0.0097 | 99.8 | 4 |
| | mg/kg | F5 | | | | | *<0.05* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.05* | 0.0005 | 0.0005 | 0.0006 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.05* | 0.0006 | 0.0006 | 0.0008 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | 0.19 | | 0.20 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS_2upper | | | | | 0.30 | 0.27 | 0.27 | 0.03 | 12.7 | 2 |
| | mg/kg | LS10lower | | | 0.19 | | 0.20 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS10upper | | | | | 0.40 | 0.33 | 0.33 | 0.10 | 30.5 | 2 |
| Ba | mg/kg | F1 | | | 0.20 | | 0.15 | 0.20 | 0.21 | 0.11 | 54.2 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.11 | 0.17 | 0.19 | 0.13 | 67.2 | 5 |
| | mg/kg | F3 | | | 0.83 | | 0.78 | 0.83 | 0.91 | 0.22 | 24.7 | 5 |
| | mg/kg | F4 | | | 1.27 | | 0.96 | 1.27 | 1.84 | 1.12 | 60.8 | 5 |
| | mg/kg | F5 | | | 37.3 | | 16.4 | 37.3 | 49.0 | 38.9 | 79.4 | 5 |
| | mg/kg | F6 | | | 209 | | 209 | 209 | 220 | 77 | 35.2 | 5 |
| | mg/kg | F7 | | | 208 | | 241 | 208 | 212 | 18 | 8.6 | 5 |
| | mg/kg | LS_2lower | | | 40.0 | | 18.4 | 40.0 | 53.4 | 43.3 | 81.1 | 3 |
| | mg/kg | LS10lower | | | 496 | | 468 | 468 | 496 | 88 | 17.7 | 3 |
| Cd | mg/kg | F1 | | | | | *<0.02* | 0.0004 | 0.0003 | 0.0001 | 42.7 | 3 |
| | mg/kg | F2 | | | | | *<0.02* | 0.0002 | 0.0005 | 0.0005 | 98.9 | 3 |
| | mg/kg | F3 | | | | | *<0.02* | 0.0004 | 0.0006 | 0.0005 | 86.8 | 3 |
| | mg/kg | F4 | | | | | *<0.02* | 0.0005 | 0.0005 | 0.0000 | 0.0 | 1 |
| | mg/kg | F5 | | | | | *<0.02* | | | | | |
| | mg/kg | F6 | | | | | *<0.02* | | | | | |
| | mg/kg | F7 | | | | | *<0.02* | | | | | |
| | mg/kg | LS_2lower | | | | | 0.0000 | 0.0004 | 0.0051 | 0.0086 | 167.3 | 3 |
| | mg/kg | LS_2upper | | | | | 0.100 | 0.023 | 0.042 | 0.051 | 121.8 | 3 |
| | mg/kg | LS10lower | | | | | 0.0000 | 0.0004 | 0.0051 | 0.0086 | 167.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.140 | 0.054 | 0.066 | 0.069 | 105.4 | 3 |
| Cl | mg/kg | F1 | | | 756 | | 731 | 756 | 675 | 298 | 44.1 | 6 |
| | mg/kg | F2 | | | 414 | | 459 | 414 | 382 | 71 | 18.7 | 5 |
| | mg/kg | F3 | | | 207 | | 357 | 207 | 227 | 93 | 40.9 | 4 |
| | mg/kg | F4 | | | 72.7 | | 120.0 | 51.0 | 72.7 | 40.7 | 56.0 | 5 |
| | mg/kg | F5 | | | 11.7 | | 17.3 | 10.0 | 11.7 | 3.3 | 28.3 | 5 |
| | mg/kg | F6 | | | 24.4 | | 22.3 | 22.5 | 24.4 | 5.0 | 20.3 | 5 |
| | mg/kg | F7 | | | 26.7 | | 20.2 | 23.6 | 26.7 | 9.5 | 35.6 | 4 |
| | mg/kg | LS_2lower | | | 1512 | | 1680 | 1552 | 1512 | 192 | 12.7 | 3 |
| | mg/kg | LS10lower | | | 1606 | | 1730 | 1606 | 1573 | 163 | 10.4 | 4 |
| Conductivity | mS/m | F1 | | | 33265 | | 29570 | 33265 | 32950 | 2642 | 8.0 | 4 |
| | mS/m | F2 | | | 34800 | | 28870 | 34800 | 33653 | 3251 | 9.7 | 4 |

| Participant 2 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Conductivity | mS/m | F3 | | | 32600 | | 28680 | 32600 | 32498 | 3053 | 9.4 | 4 |
| | mS/m | F4 | | | 15600 | | 20740 | 15600 | 16582 | 5073 | 30.6 | 5 |
| | mS/m | F5 | | | 1970 | | 3108 | 1970 | 1912 | 796 | 41.7 | 5 |
| | mS/m | F6 | | | 1122 | | 1128 | 1122 | 1119 | 46 | 4.1 | 4 |
| | mS/m | F7 | | | 753 | | 1043 | 966 | 753 | 410 | 54.5 | 5 |
| Cr | mg/kg | F1 | | | 0.41 | | 0.61 | 0.41 | 0.43 | 0.20 | 47.6 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.34 | 0.17 | 0.19 | 0.09 | 50.6 | 5 |
| | mg/kg | F3 | | | 0.26 | | 0.26 | 0.26 | 0.24 | 0.06 | 26.9 | 5 |
| | mg/kg | F4 | | | 0.075 | | 0.107 | 0.091 | 0.075 | 0.045 | 60.8 | 5 |
| | mg/kg | F5 | | | | | *<0.05* | 0.0007 | 0.0007 | 0.0003 | 42.3 | 3 |
| | mg/kg | F6 | | | | | *<0.05* | 0.0006 | 0.0006 | 0.0006 | 94.3 | 2 |
| | mg/kg | F7 | | | | | *<0.05* | | | | | |
| | mg/kg | LS_2lower | | | 0.84 | | 1.31 | 0.84 | 0.88 | 0.42 | 47.7 | 3 |
| | mg/kg | LS_2upper | | | | | 1.36 | | | | | |
| | mg/kg | LS10lower | | | 1.08 | | 1.31 | 1.08 | 1.35 | 1.00 | 74.2 | 4 |
| | mg/kg | LS10upper | | | | | 1.46 | | | | | |
| Cu | mg/kg | F1 | | | 0.11 | | 0.11 | 0.11 | 0.13 | 0.07 | 54.7 | 6 |
| | mg/kg | F2 | | | 0.088 | | 0.083 | 0.088 | 0.092 | 0.041 | 44.4 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.06 | 0.11 | 0.13 | 0.08 | 61.6 | 5 |
| | mg/kg | F4 | | | 0.042 | | *<0.05* | 0.042 | 0.048 | 0.031 | 65.8 | 4 |
| | mg/kg | F5 | | | 0.0082 | | *<0.05* | 0.0093 | 0.0082 | 0.0068 | 82.1 | 3 |
| | mg/kg | F6 | | | 0.032 | | *<0.05* | 0.046 | 0.032 | 0.026 | 81.4 | 3 |
| | mg/kg | F7 | | | 0.033 | | *<0.05* | 0.043 | 0.033 | 0.027 | 82.7 | 3 |
| | mg/kg | LS_2lower | | | 0.26 | | 0.26 | 0.26 | 0.28 | 0.12 | 43.9 | 3 |
| | mg/kg | LS_2upper | | | | | 0.36 | 3.59 | 3.59 | 4.56 | 127.2 | 2 |
| | mg/kg | LS10lower | | | 0.23 | | 0.26 | 0.23 | 0.28 | 0.15 | 53.0 | 4 |
| | mg/kg | LS10upper | | | | | 0.46 | 3.68 | 3.68 | 4.55 | 123.7 | 2 |
| F | mg/kg | F1 | | | 3.92 | | *<2* | 3.92 | 6.09 | 6.90 | 113.2 | 4 |
| | mg/kg | F2 | | | 6.04 | | *<2* | 6.41 | 6.04 | 4.16 | 69.0 | 3 |
| | mg/kg | F3 | | | 7.25 | | 2.42 | 7.25 | 7.73 | 5.89 | 76.2 | 4 |
| | mg/kg | F4 | | | 2.58 | | 3.16 | 2.58 | 2.63 | 1.54 | 58.3 | 4 |
| | mg/kg | F5 | | | 0.58 | | *<2* | 0.58 | 0.58 | 0.51 | 87.9 | 2 |
| | mg/kg | F6 | | | | | *<2* | | | | | |
| | mg/kg | F7 | | | | | *<2* | | | | | |
| | mg/kg | LS_2lower | | | 5.45 | | 5.58 | 5.45 | 5.45 | 0.18 | 3.4 | 2 |
| | mg/kg | LS_2upper | | | | | 11.60 | 9.96 | 9.96 | 2.32 | 23.3 | 2 |
| | mg/kg | LS10lower | | | 7.96 | | 5.58 | 6.90 | 7.96 | 3.05 | 38.3 | 3 |
| | mg/kg | LS10upper | | | | | 15.6 | 12.8 | 12.8 | 4.0 | 31.6 | 2 |
| Hg | mg/kg | F1 | | | | | *<0.005* | 0.0001 | 0.0017 | 0.0028 | 168.4 | 3 |
| | mg/kg | F2 | | | | | *<0.005* | 0.0001 | 0.0018 | 0.0031 | 170.3 | 3 |
| | mg/kg | F3 | | | | | *<0.005* | 0.0001 | 0.0028 | 0.0048 | 169.3 | 3 |
| | mg/kg | F4 | | | | | *<0.005* | 0.0000 | 0.0010 | 0.0018 | 170.6 | 3 |
| | mg/kg | F5 | | | | | *<0.005* | | | | | |
| | mg/kg | F6 | | | | | *<0.005* | | | | | |
| | mg/kg | F7 | | | | | *<0.005* | | | | | |
| | mg/kg | LS_2lower | | | | | 0.000 | 0.000 | 0.093 | 0.161 | 173.2 | 3 |
| | mg/kg | LS_2upper | | | | | 0.03 | 0.15 | 0.15 | 0.18 | 118.2 | 2 |
| | mg/kg | LS10lower | | | | | 0.000 | 0.000 | 0.093 | 0.161 | 173.2 | 3 |

| Participant 2 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Hg | mg/kg | LS10upper | | | | | 0.04 | 0.17 | 0.17 | 0.18 | 111.5 | 2 |
| Mo | mg/kg | F1 | | | 0.33 | | 0.42 | 0.33 | 0.30 | 0.11 | 38.6 | 6 |
| | mg/kg | F2 | | | 0.23 | | 0.23 | 0.23 | 0.25 | 0.03 | 13.7 | 5 |
| | mg/kg | F3 | | | 0.28 | | 0.27 | 0.28 | 0.28 | 0.03 | 10.6 | 4 |
| | mg/kg | F4 | | | 0.099 | | 0.149 | 0.093 | 0.099 | 0.044 | 44.7 | 5 |
| | mg/kg | F5 | | | 0.0031 | | *<0.05* | 0.0034 | 0.0031 | 0.0020 | 63.5 | 3 |
| | mg/kg | F6 | | | 0.0031 | | *<0.05* | 0.0031 | 0.0031 | 0.0001 | 4.6 | 2 |
| | mg/kg | F7 | | | 0.0040 | | *<0.05* | 0.0040 | 0.0040 | 0.0000 | 0.0 | 2 |
| | mg/kg | LS_2lower | | | 1.01 | | 1.07 | 1.01 | 1.01 | 0.06 | 5.4 | 3 |
| | mg/kg | LS_2upper | | | | | 1.12 | 6.28 | 6.28 | 7.30 | 116.2 | 2 |
| | mg/kg | LS10lower | | | 0.99 | | 1.07 | 0.99 | 1.00 | 0.05 | 5.0 | 4 |
| | mg/kg | LS10upper | | | 1.22 | | 1.22 | 1.22 | 4.59 | 6.01 | 130.9 | 3 |
| Ni | mg/kg | F1 | | | | | *<0.05* | 0.0022 | 0.0018 | 0.0007 | 38.5 | 3 |
| | mg/kg | F2 | | | | | *<0.05* | 0.0011 | 0.0008 | 0.0007 | 87.5 | 3 |
| | mg/kg | F3 | | | | | *<0.05* | 0.0010 | 0.0009 | 0.0001 | 12.4 | 3 |
| | mg/kg | F4 | | | | | *<0.05* | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F5 | | | | | *<0.05* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.05* | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.05* | 0.001 | 0.001 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | | | 0.0000 | 0.0015 | 0.0019 | 0.0022 | 120.0 | 4 |
| | mg/kg | LS_2upper | | | | | 0.25 | 0.05 | 0.10 | 0.13 | 128.7 | 3 |
| | mg/kg | LS10lower | | | | | 0.000 | 0.000 | 0.001 | 0.002 | 173.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.35 | 0.13 | 0.18 | 0.16 | 88.8 | 3 |
| Pb | mg/kg | F1 | | | 0.096 | | 0.099 | 0.096 | 0.099 | 0.030 | 30.7 | 6 |
| | mg/kg | F2 | | | 0.080 | | 0.067 | 0.077 | 0.080 | 0.015 | 18.9 | 5 |
| | mg/kg | F3 | | | 0.14 | | 0.12 | 0.14 | 0.14 | 0.02 | 15.1 | 5 |
| | mg/kg | F4 | | | 0.082 | | 0.087 | 0.084 | 0.082 | 0.012 | 14.9 | 5 |
| | mg/kg | F5 | | | 0.0095 | | *<0.05* | 0.0095 | 0.0090 | 0.0035 | 38.7 | 4 |
| | mg/kg | F6 | | | 0.016 | | *<0.05* | 0.016 | 0.016 | 0.003 | 19.1 | 4 |
| | mg/kg | F7 | | | 0.024 | | *<0.05* | 0.024 | 0.024 | 0.008 | 33.8 | 3 |
| | mg/kg | LS_2lower | | | 0.39 | | 0.37 | 0.39 | 0.39 | 0.01 | 3.5 | 3 |
| | mg/kg | LS_2upper | | | | | 0.42 | 0.42 | 0.42 | 0.00 | 0.0 | 1 |
| | mg/kg | LS10lower | | | 0.43 | | 0.37 | 0.43 | 0.42 | 0.03 | 7.5 | 4 |
| | mg/kg | LS10upper | | | | | 0.52 | 2.32 | 2.32 | 2.54 | 109.5 | 2 |
| pH | | F1 | | 1.63 | 13.6 | 3.6 | 14.0 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F2 | | 1.22 | 13.7 | 3.6 | 14.0 | 13.6 | 13.7 | 0.2 | 1.4 | 4 |
| | | F3 | | 0.81 | 13.8 | 3.6 | 14.0 | 13.8 | 13.8 | 0.2 | 1.3 | 4 |
| | | F4 | | -1.19 | 13.3 | 3.8 | 13.0 | 13.3 | 13.2 | 0.2 | 1.5 | 4 |
| | | F5 | | 0.80 | 12.8 | 3.9 | 13.0 | 12.8 | 12.8 | 0.2 | 1.4 | 6 |
| | | F6 | | 1.21 | 12.7 | 3.9 | 13.0 | 12.7 | 12.6 | 0.3 | 2.1 | 6 |
| | | F7 | | 1.21 | 12.7 | 3.9 | 13.0 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |
| Sb | mg/kg | F1 | | | 0.0035 | | *<0.03* | 0.0020 | 0.0035 | 0.0026 | 75.8 | 3 |
| | mg/kg | F2 | | | 0.0019 | | *<0.03* | 0.0020 | 0.0019 | 0.0005 | 24.1 | 3 |
| | mg/kg | F3 | | | 0.0087 | | *<0.03* | 0.0030 | 0.0087 | 0.0106 | 121.7 | 3 |
| | mg/kg | F4 | | | 0.0031 | | *<0.03* | 0.0010 | 0.0031 | 0.0036 | 117.3 | 3 |
| | mg/kg | F5 | | | | | *<0.03* | 0.0021 | 0.0021 | 0.0030 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.03* | 0.0046 | 0.0046 | 0.0065 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.03* | 0.0055 | 0.0055 | 0.0078 | 141.4 | 2 |

| Participant 2 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Sb | mg/kg | LS_2lower | | | | | 0.0000 | 0.0033 | 0.0034 | 0.0039 | 115.6 | 4 |
| | mg/kg | LS_2upper | | | | | 0.150 | 0.048 | 0.068 | 0.074 | 108.1 | 3 |
| | mg/kg | LS10lower | | | | | 0.0000 | 0.0000 | 0.0023 | 0.0040 | 173.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.21 | 0.17 | 0.17 | 0.06 | 34.8 | 2 |
| Se | mg/kg | F1 | | | 0.049 | | 0.075 | 0.050 | 0.049 | 0.022 | 44.5 | 5 |
| | mg/kg | F2 | | | 0.025 | | *<0.05* | 0.025 | 0.025 | 0.006 | 25.0 | 4 |
| | mg/kg | F3 | | | 0.032 | | 0.053 | 0.025 | 0.032 | 0.017 | 53.7 | 5 |
| | mg/kg | F4 | | | 0.0047 | | *<0.05* | 0.0047 | 0.0066 | 0.0060 | 91.5 | 4 |
| | mg/kg | F5 | | | | | *<0.05* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.05* | | | | | |
| | mg/kg | F7 | | | | | *<0.05* | 0.002 | 0.002 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | 0.11 | | 0.13 | 0.12 | 0.11 | 0.02 | 19.6 | 3 |
| | mg/kg | LS_2upper | | | | | 0.28 | 0.20 | 0.20 | 0.11 | 53.7 | 2 |
| | mg/kg | LS10lower | | | 0.11 | | 0.13 | 0.12 | 0.11 | 0.02 | 18.5 | 3 |
| | mg/kg | LS10upper | | | | | 0.38 | 0.38 | 0.38 | 0.23 | 60.1 | 3 |
| $SO_4$ | mg/kg | F1 | | | 2350 | | 2200 | 2350 | 2332 | 660 | 28.3 | 6 |
| | mg/kg | F2 | | | 2300 | | 2300 | 2300 | 2444 | 565 | 23.1 | 5 |
| | mg/kg | F3 | | | 5990 | | 6080 | 5990 | 5718 | 895 | 15.6 | 5 |
| | mg/kg | F4 | | | 2813 | | 3240 | 2813 | 2273 | 1516 | 66.7 | 5 |
| | mg/kg | F5 | | | 6.96 | | 385.00 | 6.96 | 8.93 | 6.99 | 78.3 | 4 |
| | mg/kg | F6 | | | 4.93 | | 4.76 | 4.93 | 8.46 | 9.72 | 114.9 | 4 |
| | mg/kg | F7 | | | 7.31 | | 8.50 | 8.50 | 7.31 | 2.06 | 28.2 | 3 |
| | mg/kg | LS_2lower | | | 13206 | | 14204 | 14160 | 13206 | 1691 | 12.8 | 3 |
| | mg/kg | LS10lower | | | 13290 | | 14217 | 13290 | 13016 | 1442 | 11.1 | 4 |
| V | mg/kg | F1 | | | 0.13 | | 0.16 | 0.13 | 0.12 | 0.05 | 38.3 | 5 |
| | mg/kg | F2 | | | 0.10 | | 0.10 | 0.10 | 0.10 | 0.04 | 35.6 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.10 | 0.11 | 0.11 | 0.03 | 30.6 | 4 |
| | mg/kg | F4 | | | 0.020 | | *<0.05* | 0.020 | 0.035 | 0.038 | 107.6 | 4 |
| | mg/kg | F5 | | | | | *<0.05* | | | | | |
| | mg/kg | F6 | | | | | *<0.05* | | | | | |
| | mg/kg | F7 | | | | | *<0.05* | | | | | |
| | mg/kg | LS_2lower | | | 0.36 | | 0.36 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| | mg/kg | LS_2upper | | | | | 0.46 | 0.48 | 2.33 | 3.22 | 138.2 | 3 |
| | mg/kg | LS10lower | | | 0.36 | | 0.36 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| | mg/kg | LS10upper | | | | | 0.56 | 0.56 | 2.39 | 3.24 | 135.3 | 3 |
| Zn | mg/kg | F1 | | | 94.0 | | 113.0 | 94.0 | 98.4 | 41.0 | 41.6 | 5 |
| | mg/kg | F2 | | | 79.8 | | 82.0 | 79.8 | 78.2 | 22.5 | 28.7 | 4 |
| | mg/kg | F3 | | | 106 | | 74 | 106 | 110 | 47 | 42.7 | 4 |
| | mg/kg | F4 | | | 31.7 | | 46.4 | 31.7 | 33.8 | 23.8 | 70.4 | 4 |
| | mg/kg | F5 | | | 0.78 | | 2.21 | 0.78 | 0.99 | 0.87 | 87.6 | 4 |
| | mg/kg | F6 | | | 0.66 | | 0.94 | 0.66 | 0.73 | 0.44 | 59.9 | 4 |
| | mg/kg | F7 | | | 0.74 | | 1.02 | 0.74 | 0.74 | 0.31 | 41.3 | 4 |
| | mg/kg | LS_2lower | | | 260 | | 318 | 260 | 260 | 82 | 31.5 | 2 |
| | mg/kg | LS10lower | | | 278 | | 320 | 312 | 278 | 65 | 23.5 | 3 |

| Participant 3 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| As | mg/kg | F1 | | | 0.074 | | 0.097 | 0.074 | 0.074 | 0.035 | 47.2 | 6 |
| | mg/kg | F2 | | | 0.050 | | 0.041 | 0.050 | 0.047 | 0.015 | 32.1 | 5 |
| | mg/kg | F3 | | | 0.051 | | 0.027 | 0.051 | 0.055 | 0.031 | 57.5 | 5 |
| | mg/kg | F4 | | | 0.0097 | | 0.0047 | 0.0059 | 0.0097 | 0.0097 | 99.8 | 4 |
| | mg/kg | F5 | | | | | 0.0002 | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0.0009 | 0.0005 | 0.0005 | 0.0006 | 141.4 | 2 |
| | mg/kg | F7 | | | | | 0.0011 | 0.0006 | 0.0006 | 0.0008 | 141.4 | 2 |
| Ba | mg/kg | F1 | | | 0.20 | | 0.04 | 0.20 | 0.21 | 0.11 | 54.2 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.04 | 0.17 | 0.19 | 0.13 | 67.2 | 5 |
| | mg/kg | F3 | | | 0.83 | | 0.67 | 0.83 | 0.91 | 0.22 | 24.7 | 5 |
| | mg/kg | F4 | | | 1.27 | | 3.40 | 1.27 | 1.84 | 1.12 | 60.8 | 5 |
| | mg/kg | F5 | | | 37.3 | | 81.6 | 37.3 | 49.0 | 38.9 | 79.4 | 5 |
| | mg/kg | F6 | | | 209 | | 109 | 209 | 220 | 77 | 35.2 | 5 |
| | mg/kg | F7 | | | 208 | | 206 | 208 | 212 | 18 | 8.6 | 5 |
| Cd | mg/kg | F1 | | | | | 0.0005 | 0.0004 | 0.0003 | 0.0001 | 42.7 | 3 |
| | mg/kg | F2 | | | | | 0.0002 | 0.0002 | 0.0005 | 0.0005 | 98.9 | 3 |
| | mg/kg | F3 | | | | | 0.0004 | 0.0004 | 0.0006 | 0.0005 | 86.8 | 3 |
| | mg/kg | F4 | | | | | *<0.00005* | 0.0005 | 0.0005 | 0.0000 | 0.0 | 1 |
| | mg/kg | F5 | | | | | *<0.0001* | | | | | |
| | mg/kg | F6 | | | | | *<0.0003* | | | | | |
| | mg/kg | F7 | | | | | *<0.0005* | | | | | |
| Cl | mg/kg | F1 | | | 756 | | 1018 | 756 | 675 | 298 | 44.1 | 6 |
| | mg/kg | F2 | | | 414 | | 340 | 414 | 382 | 71 | 18.7 | 5 |
| | mg/kg | F3 | | | 207 | | 137 | 207 | 227 | 93 | 40.9 | 4 |
| | mg/kg | F4 | | | 72.7 | | 51.0 | 51.0 | 72.7 | 40.7 | 56.0 | 5 |
| | mg/kg | F5 | | | 11.7 | | 12.0 | 10.0 | 11.7 | 3.3 | 28.3 | 5 |
| | mg/kg | F6 | | | 24.4 | | 32.0 | 22.5 | 24.4 | 5.0 | 20.3 | 5 |
| | mg/kg | F7 | | | 26.7 | | 40.0 | 23.6 | 26.7 | 9.5 | 35.6 | 4 |
| Conductivity | mS/m | F1 | | | 33265 | | 54300 | 33265 | 32950 | 2642 | 8.0 | 4 |
| | mS/m | F2 | | | 34800 | | 53000 | 34800 | 33653 | 3251 | 9.7 | 4 |
| | mS/m | F3 | | | 32600 | | 56300 | 32600 | 32498 | 3053 | 9.4 | 4 |
| | mS/m | F4 | | | 15600 | | 15600 | 15600 | 16582 | 5073 | 30.6 | 5 |
| | mS/m | F5 | | | 1970 | | 1970 | 1970 | 1912 | 796 | 41.7 | 5 |
| | mS/m | F6 | | | 1122 | | 1060 | 1122 | 1119 | 46 | 4.1 | 4 |
| | mS/m | F7 | | | 753 | | 966 | 966 | 753 | 410 | 54.5 | 5 |
| Cr | mg/kg | F1 | | | 0.41 | | 0.54 | 0.41 | 0.43 | 0.20 | 47.6 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.17 | 0.17 | 0.19 | 0.09 | 50.6 | 5 |
| | mg/kg | F3 | | | 0.26 | | 0.22 | 0.26 | 0.24 | 0.06 | 26.9 | 5 |
| | mg/kg | F4 | | | 0.075 | | 0.032 | 0.091 | 0.075 | 0.045 | 60.8 | 5 |
| | mg/kg | F5 | | | | | 0.0004 | 0.0007 | 0.0007 | 0.0003 | 42.3 | 3 |
| | mg/kg | F6 | | | | | 0.0002 | 0.0006 | 0.0006 | 0.0006 | 94.3 | 2 |
| | mg/kg | F7 | | | | | *<0.0002* | | | | | |
| Cu | mg/kg | F1 | | | 0.11 | | 0.27 | 0.11 | 0.13 | 0.07 | 54.7 | 6 |
| | mg/kg | F2 | | | 0.088 | | 0.118 | 0.088 | 0.092 | 0.041 | 44.4 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.16 | 0.11 | 0.13 | 0.08 | 61.6 | 5 |
| | mg/kg | F4 | | | 0.042 | | 0.036 | 0.042 | 0.048 | 0.031 | 65.8 | 4 |
| | mg/kg | F5 | | | 0.0082 | | 0.0144 | 0.0093 | 0.0082 | 0.0068 | 82.1 | 3 |
| | mg/kg | F6 | | | 0.032 | | 0.046 | 0.046 | 0.032 | 0.026 | 81.4 | 3 |

| Participant 3 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Cu | mg/kg | F7 | | | 0.033 | | 0.053 | 0.043 | 0.033 | 0.027 | 82.7 | 3 |
| DOC | mg/kg | F1 | | | 420 | | 906 | 420 | 475 | 375 | 78.9 | 4 |
| | mg/kg | F2 | | | 396 | | 480 | 480 | 396 | 200 | 50.5 | 3 |
| | mg/kg | F3 | | | 926 | | 1003 | 1003 | 926 | 557 | 60.2 | 3 |
| | mg/kg | F4 | | | 279 | | 297 | 297 | 279 | 211 | 75.9 | 3 |
| | mg/kg | F5 | | | 18.8 | | 24.0 | 22.9 | 18.8 | 8.1 | 42.9 | 3 |
| | mg/kg | F6 | | | 41.0 | | 43.0 | 43.0 | 41.0 | 24.4 | 59.6 | 3 |
| | mg/kg | F7 | | | 62.0 | | 57.0 | 57.0 | 62.0 | 33.3 | 53.7 | 3 |
| F | mg/kg | F1 | | | 3.92 | | 16.00 | 3.92 | 6.09 | 6.90 | 113.2 | 4 |
| | mg/kg | F2 | | | 6.04 | | 10.00 | 6.41 | 6.04 | 4.16 | 69.0 | 3 |
| | mg/kg | F3 | | | 7.25 | | 14.00 | 7.25 | 7.73 | 5.89 | 76.2 | 4 |
| | mg/kg | F4 | | | 2.58 | | 2.00 | 2.58 | 2.63 | 1.54 | 58.3 | 4 |
| | mg/kg | F5 | | | 0.58 | | <2 | 0.58 | 0.58 | 0.51 | 87.9 | 2 |
| | mg/kg | F6 | | | | | <2 | | | | | |
| | mg/kg | F7 | | | | | <2 | | | | | |
| Hg | mg/kg | F1 | | | | | 0.0001 | 0.0001 | 0.0017 | 0.0028 | 168.4 | 3 |
| | mg/kg | F2 | | | | | 0.0001 | 0.0001 | 0.0018 | 0.0031 | 170.3 | 3 |
| | mg/kg | F3 | | | | | 0.0001 | 0.0001 | 0.0028 | 0.0048 | 169.3 | 3 |
| | mg/kg | F4 | | | | | 0.0000 | 0.0000 | 0.0010 | 0.0018 | 170.6 | 3 |
| | mg/kg | F5 | | | | | *<0.0001* | | | | | |
| | mg/kg | F6 | | | | | *<0.0003* | | | | | |
| | mg/kg | F7 | | | | | *<0.0005* | | | | | |
| Mo | mg/kg | F1 | | | 0.33 | | 0.29 | 0.33 | 0.30 | 0.11 | 38.6 | 6 |
| | mg/kg | F2 | | | 0.23 | | 0.22 | 0.23 | 0.25 | 0.03 | 13.7 | 5 |
| | mg/kg | F3 | | | 0.28 | | 0.28 | 0.28 | 0.28 | 0.03 | 10.6 | 4 |
| | mg/kg | F4 | | | 0.099 | | 0.070 | 0.093 | 0.099 | 0.044 | 44.7 | 5 |
| | mg/kg | F5 | | | 0.0031 | | 0.0049 | 0.0034 | 0.0031 | 0.0020 | 63.5 | 3 |
| | mg/kg | F6 | | | 0.0031 | | 0.0032 | 0.0031 | 0.0031 | 0.0001 | 4.6 | 2 |
| | mg/kg | F7 | | | 0.0040 | | 0.0040 | 0.0040 | 0.0040 | 0.0000 | 0.0 | 2 |
| Ni | mg/kg | F1 | | | | | 0.0022 | 0.0022 | 0.0018 | 0.0007 | 38.5 | 3 |
| | mg/kg | F2 | | | | | 0.0011 | 0.0011 | 0.0008 | 0.0007 | 87.5 | 3 |
| | mg/kg | F3 | | | | | 0.0008 | 0.0010 | 0.0009 | 0.0001 | 12.4 | 3 |
| | mg/kg | F4 | | | | | 0.0003 | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F5 | | | | | 0.0002 | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0.0003 | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.0002* | 0.001 | 0.001 | 0.000 | 0.0 | 1 |
| Pb | mg/kg | F1 | | | 0.096 | | 0.150 | 0.096 | 0.099 | 0.030 | 30.7 | 6 |
| | mg/kg | F2 | | | 0.080 | | 0.106 | 0.077 | 0.080 | 0.015 | 18.9 | 5 |
| | mg/kg | F3 | | | 0.14 | | 0.11 | 0.14 | 0.14 | 0.02 | 15.1 | 5 |
| | mg/kg | F4 | | | 0.082 | | 0.084 | 0.084 | 0.082 | 0.012 | 14.9 | 5 |
| | mg/kg | F5 | | | 0.0095 | | 0.0125 | 0.0095 | 0.0090 | 0.0035 | 38.7 | 4 |
| | mg/kg | F6 | | | 0.016 | | 0.013 | 0.016 | 0.016 | 0.003 | 19.1 | 4 |
| | mg/kg | F7 | | | 0.024 | | 0.016 | 0.024 | 0.024 | 0.008 | 33.8 | 3 |
| pH | | F1 | | -4.08 | 13.6 | 3.6 | 12.6 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F2 | | -3.65 | 13.7 | 3.6 | 12.8 | 13.6 | 13.7 | 0.2 | 1.4 | 4 |
| | | F3 | | -4.43 | 13.8 | 3.6 | 12.7 | 13.8 | 13.8 | 0.2 | 1.3 | 4 |
| | | F4 | | -2.37 | 13.3 | 3.8 | 12.7 | 13.3 | 13.2 | 0.2 | 1.5 | 4 |
| | | F5 | | -0.80 | 12.8 | 3.9 | 12.6 | 12.8 | 12.8 | 0.2 | 1.4 | 6 |

| Participant 3 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| pH | | F6 | | -1.62 | 12.7 | 3.9 | 12.3 | 12.7 | 12.6 | 0.3 | 2.1 | 6 |
| | | F7 | | -1.62 | 12.7 | 3.9 | 12.3 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |
| Sb | mg/kg | F1 | | | 0.0035 | | 0.0065 | 0.0020 | 0.0035 | 0.0026 | 75.8 | 3 |
| | mg/kg | F2 | | | 0.0019 | | 0.0023 | 0.0020 | 0.0019 | 0.0005 | 24.1 | 3 |
| | mg/kg | F3 | | | 0.0087 | | 0.0210 | 0.0030 | 0.0087 | 0.0106 | 121.7 | 3 |
| | mg/kg | F4 | | | 0.0031 | | 0.0073 | 0.0010 | 0.0031 | 0.0036 | 117.3 | 3 |
| | mg/kg | F5 | | | | | 0.0042 | 0.0021 | 0.0021 | 0.0030 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0.0092 | 0.0046 | 0.0046 | 0.0065 | 141.4 | 2 |
| | mg/kg | F7 | | | | | 0.0110 | 0.0055 | 0.0055 | 0.0078 | 141.4 | 2 |
| Se | mg/kg | F1 | | | 0.049 | | 0.050 | 0.050 | 0.049 | 0.022 | 44.5 | 5 |
| | mg/kg | F2 | | | 0.025 | | 0.020 | 0.025 | 0.025 | 0.006 | 25.0 | 4 |
| | mg/kg | F3 | | | 0.032 | | 0.014 | 0.025 | 0.032 | 0.017 | 53.7 | 5 |
| | mg/kg | F4 | | | 0.0047 | | 0.0024 | 0.0047 | 0.0066 | 0.0060 | 91.5 | 4 |
| | mg/kg | F5 | | | | | 0.0002 | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.0007* | | | | | |
| | mg/kg | F7 | | | | | *<0.0012* | 0.002 | 0.002 | 0.000 | 0.0 | 1 |
| $SO_4$ | mg/kg | F1 | | | 2350 | | 3100 | 2350 | 2332 | 660 | 28.3 | 6 |
| | mg/kg | F2 | | | 2300 | | 3000 | 2300 | 2444 | 565 | 23.1 | 5 |
| | mg/kg | F3 | | | 5990 | | 5990 | 5990 | 5718 | 895 | 15.6 | 5 |
| | mg/kg | F4 | | | 2813 | | 600 | 2813 | 2273 | 1516 | 66.7 | 5 |
| | mg/kg | F5 | | | 6.96 | | 10.00 | 6.96 | 8.93 | 6.99 | 78.3 | 4 |
| | mg/kg | F6 | | | 4.93 | | *<20* | 4.93 | 8.46 | 9.72 | 114.9 | 4 |
| | mg/kg | F7 | | | 7.31 | | *<30* | 8.50 | 7.31 | 2.06 | 28.2 | 3 |
| V | mg/kg | F1 | | | 0.13 | | 0.11 | 0.13 | 0.12 | 0.05 | 38.3 | 5 |
| | mg/kg | F2 | | | 0.10 | | 0.05 | 0.10 | 0.10 | 0.04 | 35.6 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.07 | 0.11 | 0.11 | 0.03 | 30.6 | 4 |
| | mg/kg | F4 | | | 0.020 | | 0.010 | 0.020 | 0.035 | 0.038 | 107.6 | 4 |
| | mg/kg | F5 | | | | | *<0.0005* | | | | | |
| | mg/kg | F6 | | | | | *<0.002* | | | | | |
| | mg/kg | F7 | | | | | *<0.003* | | | | | |
| Zn | mg/kg | F1 | | | 94.0 | | 159.0 | 94.0 | 98.4 | 41.0 | 41.6 | 5 |
| | mg/kg | F2 | | | 79.8 | | 104.0 | 79.8 | 78.2 | 22.5 | 28.7 | 4 |
| | mg/kg | F3 | | | 106 | | 137 | 106 | 110 | 47 | 42.7 | 4 |
| | mg/kg | F4 | | | 31.7 | | 17.0 | 31.7 | 33.8 | 23.8 | 70.4 | 4 |
| | mg/kg | F5 | | | 0.78 | | 0.67 | 0.78 | 0.99 | 0.87 | 87.6 | 4 |
| | mg/kg | F6 | | | 0.66 | | 0.35 | 0.66 | 0.73 | 0.44 | 59.9 | 4 |
| | mg/kg | F7 | | | 0.74 | | 0.46 | 0.74 | 0.74 | 0.31 | 41.3 | 4 |

| Participant 4 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Conductivity | mS/m | F1 | | | 33265 | | 35700 | 33265 | 32950 | 2642 | 8.0 | 4 |
| | mS/m | F2 | | | 34800 | | 34700 | 34800 | 33653 | 3251 | 9.7 | 4 |
| | mS/m | F3 | | | 32600 | | 32200 | 32600 | 32498 | 3053 | 9.4 | 4 |
| | mS/m | F4 | | | 15600 | | 12100 | 15600 | 16582 | 5073 | 30.6 | 5 |
| | mS/m | F5 | | | 1970 | | 1010 | 1970 | 1912 | 796 | 41.7 | 5 |
| | mS/m | F6 | | | 1122 | | 488 | 1122 | 1119 | 46 | 4.1 | 4 |
| | mS/m | F7 | | | 753 | | 583 | 966 | 753 | 410 | 54.5 | 5 |

| Participant 4 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| pH | | F1 | | 0.41 | 13.6 | 3.6 | 13.7 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F2 | | -0.41 | 13.7 | 3.6 | 13.6 | 13.6 | 13.7 | 0.2 | 1.4 | 4 |
| | | F3 | | -0.40 | 13.8 | 3.6 | 13.7 | 13.8 | 13.8 | 0.2 | 1.3 | 4 |
| | | F4 | | 0.40 | 13.3 | 3.8 | 13.4 | 13.3 | 13.2 | 0.2 | 1.5 | 4 |
| | | F5 | | 0.00 | 12.8 | 3.9 | 12.8 | 12.8 | 12.8 | 0.2 | 1.4 | 6 |
| | | F6 | | -1.21 | 12.7 | 3.9 | 12.4 | 12.7 | 12.6 | 0.3 | 2.1 | 6 |
| | | F7 | | -1.21 | 12.7 | 3.9 | 12.4 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| As | mg/kg | F1 | | | 0.074 | | 0.027 | 0.074 | 0.074 | 0.035 | 47.2 | 6 |
| | mg/kg | F2 | | | 0.050 | | 0.050 | 0.050 | 0.047 | 0.015 | 32.1 | 5 |
| | mg/kg | F3 | | | 0.051 | | 0.107 | 0.051 | 0.055 | 0.031 | 57.5 | 5 |
| | mg/kg | F4 | | | 0.0097 | | 0.0240 | 0.0059 | 0.0097 | 0.0097 | 99.8 | 4 |
| | mg/kg | F5 | | | | | *<0.005* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.005* | 0.0005 | 0.0005 | 0.0006 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | 0.0006 | 0.0006 | 0.0008 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | 0.19 | | 2.23 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS_2upper | | | | | 2.24 | 0.27 | 0.27 | 0.03 | 12.7 | 2 |
| | mg/kg | LS10lower | | | 0.19 | | 2.23 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS10upper | | | | | 2.32 | 0.33 | 0.33 | 0.10 | 30.5 | 2 |
| Ba | mg/kg | F1 | | | 0.20 | | 0.18 | 0.20 | 0.21 | 0.11 | 54.2 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.17 | 0.17 | 0.19 | 0.13 | 67.2 | 5 |
| | mg/kg | F3 | | | 0.83 | | 1.24 | 0.83 | 0.91 | 0.22 | 24.7 | 5 |
| | mg/kg | F4 | | | 1.27 | | 1.27 | 1.27 | 1.84 | 1.12 | 60.8 | 5 |
| | mg/kg | F5 | | | 37.3 | | 11.6 | 37.3 | 49.0 | 38.9 | 79.4 | 5 |
| | mg/kg | F6 | | | 209 | | 306 | 209 | 220 | 77 | 35.2 | 5 |
| | mg/kg | F7 | | | 208 | | 208 | 208 | 212 | 18 | 8.6 | 5 |
| | mg/kg | LS_2lower | | | 40.0 | | 43.9 | 40.0 | 53.4 | 43.3 | 81.1 | 3 |
| | mg/kg | LS10lower | | | 496 | | 1189 | 468 | 496 | 88 | 17.7 | 3 |
| Cd | mg/kg | F1 | | | | | *<0.002* | 0.0004 | 0.0003 | 0.0001 | 42.7 | 3 |
| | mg/kg | F2 | | | | | *<0.002* | 0.0002 | 0.0005 | 0.0005 | 98.9 | 3 |
| | mg/kg | F3 | | | | | *<0.002* | 0.0004 | 0.0006 | 0.0005 | 86.8 | 3 |
| | mg/kg | F4 | | | | | *<0.002* | 0.0005 | 0.0005 | 0.0000 | 0.0 | 1 |
| | mg/kg | F5 | | | | | *<0.002* | | | | | |
| | mg/kg | F6 | | | | | *<0.002* | | | | | |
| | mg/kg | F7 | | | | | *<0.002* | | | | | |
| | mg/kg | LS_2lower | | | | | 0.0150 | 0.0004 | 0.0051 | 0.0086 | 167.3 | 3 |
| | mg/kg | LS_2upper | | | | | 0.023 | 0.023 | 0.042 | 0.051 | 121.8 | 3 |
| | mg/kg | LS10lower | | | | | 0.0150 | 0.0004 | 0.0051 | 0.0086 | 167.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.054 | 0.054 | 0.066 | 0.069 | 105.4 | 3 |
| Cl | mg/kg | F1 | | | 756 | | 203 | 756 | 675 | 298 | 44.1 | 6 |
| | mg/kg | F2 | | | 414 | | 417 | 414 | 382 | 71 | 18.7 | 5 |
| | mg/kg | F3 | | | 207 | | 791 | 207 | 227 | 93 | 40.9 | 4 |
| | mg/kg | F4 | | | 72.7 | | 112.9 | 51.0 | 72.7 | 40.7 | 56.0 | 5 |
| | mg/kg | F5 | | | 11.7 | | 9.8 | 10.0 | 11.7 | 3.3 | 28.3 | 5 |
| | mg/kg | F6 | | | 24.4 | | 22.5 | 22.5 | 24.4 | 5.0 | 20.3 | 5 |
| | mg/kg | F7 | | | 26.7 | | 27.1 | 23.6 | 26.7 | 9.5 | 35.6 | 4 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Cl | mg/kg | LS_2lower | | | 1512 | | 17120 | 1552 | 1512 | 192 | 12.7 | 3 |
| | mg/kg | LS10lower | | | 1606 | | 17223 | 1606 | 1573 | 163 | 10.4 | 4 |
| Conductivity | mS/m | F1 | | | 33265 | | 32330 | 33265 | 32950 | 2642 | 8.0 | 4 |
| | mS/m | F2 | | | 34800 | | 36140 | 34800 | 33653 | 3251 | 9.7 | 4 |
| | mS/m | F3 | | | 32600 | | 36110 | 32600 | 32498 | 3053 | 9.4 | 4 |
| | mS/m | F4 | | | 15600 | | 22880 | 15600 | 16582 | 5073 | 30.6 | 5 |
| | mS/m | F5 | | | 1970 | | 2071 | 1970 | 1912 | 796 | 41.7 | 5 |
| | mS/m | F6 | | | 1122 | | 1172 | 1122 | 1119 | 46 | 4.1 | 4 |
| | mS/m | F7 | | | 753 | | 107 | 966 | 753 | 410 | 54.5 | 5 |
| Cr | mg/kg | F1 | | | 0.41 | | 0.22 | 0.41 | 0.43 | 0.20 | 47.6 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.16 | 0.17 | 0.19 | 0.09 | 50.6 | 5 |
| | mg/kg | F3 | | | 0.26 | | 0.29 | 0.26 | 0.24 | 0.06 | 26.9 | 5 |
| | mg/kg | F4 | | | 0.075 | | 0.122 | 0.091 | 0.075 | 0.045 | 60.8 | 5 |
| | mg/kg | F5 | | | | | *<0.005* | 0.0007 | 0.0007 | 0.0003 | 42.3 | 3 |
| | mg/kg | F6 | | | | | *<0.005* | 0.0006 | 0.0006 | 0.0006 | 94.3 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | | | | | |
| | mg/kg | LS_2lower | | | 0.84 | | 10.13 | 0.84 | 0.88 | 0.42 | 47.7 | 3 |
| | mg/kg | LS_2upper | | | | | 10.14 | | | | | |
| | mg/kg | LS10lower | | | 1.08 | | 10.13 | 1.08 | 1.35 | 1.00 | 74.2 | 4 |
| | mg/kg | LS10upper | | | | | 10.22 | | | | | |
| Cu | mg/kg | F1 | | | 0.11 | | 0.11 | 0.11 | 0.13 | 0.07 | 54.7 | 6 |
| | mg/kg | F2 | | | 0.088 | | 0.138 | 0.088 | 0.092 | 0.041 | 44.4 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.25 | 0.11 | 0.13 | 0.08 | 61.6 | 5 |
| | mg/kg | F4 | | | 0.042 | | 0.090 | 0.042 | 0.048 | 0.031 | 65.8 | 4 |
| | mg/kg | F5 | | | 0.0082 | | *<0.005* | 0.0093 | 0.0082 | 0.0068 | 82.1 | 3 |
| | mg/kg | F6 | | | 0.032 | | *<0.009* | 0.046 | 0.032 | 0.026 | 81.4 | 3 |
| | mg/kg | F7 | | | 0.033 | | *<0.009* | 0.043 | 0.033 | 0.027 | 82.7 | 3 |
| | mg/kg | LS_2lower | | | 0.26 | | 6.80 | 0.26 | 0.28 | 0.12 | 43.9 | 3 |
| | mg/kg | LS_2upper | | | | | 6.81 | 3.59 | 3.59 | 4.56 | 127.2 | 2 |
| | mg/kg | LS10lower | | | 0.23 | | 6.80 | 0.23 | 0.28 | 0.15 | 53.0 | 4 |
| | mg/kg | LS10upper | | | | | 6.89 | 3.68 | 3.68 | 4.55 | 123.7 | 2 |
| DOC | mg/kg | F1 | | | 420 | | 152 | 420 | 475 | 375 | 78.9 | 4 |
| | mg/kg | F2 | | | 396 | | 168 | 480 | 396 | 200 | 50.5 | 3 |
| | mg/kg | F3 | | | 926 | | 334 | 1003 | 926 | 557 | 60.2 | 3 |
| | mg/kg | F4 | | | 279 | | 59 | 297 | 279 | 211 | 75.9 | 3 |
| | mg/kg | F5 | | | 18.8 | | 22.9 | 22.9 | 18.8 | 8.1 | 42.9 | 3 |
| | mg/kg | F6 | | | 41.0 | | 64.3 | 43.0 | 41.0 | 24.4 | 59.6 | 3 |
| | mg/kg | F7 | | | 62.0 | | 97.5 | 57.0 | 62.0 | 33.3 | 53.7 | 3 |
| | mg/kg | LS_2lower | | | | | 8789 | 5964 | 5964 | 3995 | 67.0 | 2 |
| | mg/kg | LS10lower | | | 4309 | | 9116 | 3187 | 4309 | 4355 | 101.1 | 3 |
| F | mg/kg | F1 | | | 3.92 | | 5.34 | 3.92 | 6.09 | 6.90 | 113.2 | 4 |
| | mg/kg | F2 | | | 6.04 | | 6.41 | 6.41 | 6.04 | 4.16 | 69.0 | 3 |
| | mg/kg | F3 | | | 7.25 | | 11.50 | 7.25 | 7.73 | 5.89 | 76.2 | 4 |
| | mg/kg | F4 | | | 2.58 | | 4.47 | 2.58 | 2.63 | 1.54 | 58.3 | 4 |
| | mg/kg | F5 | | | 0.58 | | 0.94 | 0.58 | 0.58 | 0.51 | 87.9 | 2 |
| | mg/kg | F6 | | | | | 1.749 | | | | | |
| | mg/kg | F7 | | | | | 2.315 | | | | | |
| | mg/kg | LS_2lower | | | 5.45 | | 325.03 | 5.45 | 5.45 | 0.18 | 3.4 | 2 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| F | mg/kg | LS10lower | | | 7.96 | | 333.39 | 6.90 | 7.96 | 3.05 | 38.3 | 3 |
| Hg | mg/kg | F1 | | | | | 0.0049 | 0.0001 | 0.0017 | 0.0028 | 168.4 | 3 |
| | mg/kg | F2 | | | | | 0.0054 | 0.0001 | 0.0018 | 0.0031 | 170.3 | 3 |
| | mg/kg | F3 | | | | | 0.0084 | 0.0001 | 0.0028 | 0.0048 | 169.3 | 3 |
| | mg/kg | F4 | | | | | 0.0031 | 0.0000 | 0.0010 | 0.0018 | 170.6 | 3 |
| | mg/kg | F5 | | | | | *<0.001* | | | | | |
| | mg/kg | F6 | | | | | *<0.001* | | | | | |
| | mg/kg | F7 | | | | | *<0.001* | | | | | |
| | mg/kg | LS_2lower | | | | | 0.278 | 0.000 | 0.093 | 0.161 | 173.2 | 3 |
| | mg/kg | LS_2upper | | | | | 0.28 | 0.15 | 0.15 | 0.18 | 118.2 | 2 |
| | mg/kg | LS10lower | | | | | 0.278 | 0.000 | 0.093 | 0.161 | 173.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.30 | 0.17 | 0.17 | 0.18 | 111.5 | 2 |
| Mo | mg/kg | F1 | | | 0.33 | | 0.14 | 0.33 | 0.30 | 0.11 | 38.6 | 6 |
| | mg/kg | F2 | | | 0.23 | | 0.27 | 0.23 | 0.25 | 0.03 | 13.7 | 5 |
| | mg/kg | F3 | | | 0.28 | | 0.51 | 0.28 | 0.28 | 0.03 | 10.6 | 4 |
| | mg/kg | F4 | | | 0.099 | | 0.138 | 0.093 | 0.099 | 0.044 | 44.7 | 5 |
| | mg/kg | F5 | | | 0.0031 | | *<0.005* | 0.0034 | 0.0031 | 0.0020 | 63.5 | 3 |
| | mg/kg | F6 | | | 0.0031 | | *<0.005* | 0.0031 | 0.0031 | 0.0001 | 4.6 | 2 |
| | mg/kg | F7 | | | 0.0040 | | *<0.005* | 0.0040 | 0.0040 | 0.0000 | 0.0 | 2 |
| | mg/kg | LS_2lower | | | 1.01 | | 11.43 | 1.01 | 1.01 | 0.06 | 5.4 | 3 |
| | mg/kg | LS_2upper | | | | | 11.44 | 6.28 | 6.28 | 7.30 | 116.2 | 2 |
| | mg/kg | LS10lower | | | 0.99 | | 11.43 | 0.99 | 1.00 | 0.05 | 5.0 | 4 |
| | mg/kg | LS10upper | | | 1.22 | | 11.52 | 1.22 | 4.59 | 6.01 | 130.9 | 3 |
| Ni | mg/kg | F1 | | | | | *<0.005* | 0.0022 | 0.0018 | 0.0007 | 38.5 | 3 |
| | mg/kg | F2 | | | | | *<0.005* | 0.0011 | 0.0008 | 0.0007 | 87.5 | 3 |
| | mg/kg | F3 | | | | | *<0.005* | 0.0010 | 0.0009 | 0.0001 | 12.4 | 3 |
| | mg/kg | F4 | | | | | *<0.005* | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F5 | | | | | *<0.005* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.005* | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | 0.001 | 0.001 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | | | 0.0000 | 0.0015 | 0.0019 | 0.0022 | 120.0 | 4 |
| | mg/kg | LS_2upper | | | | | 0.05 | 0.05 | 0.10 | 0.13 | 128.7 | 3 |
| | mg/kg | LS10lower | | | | | 0.000 | 0.000 | 0.001 | 0.002 | 173.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.13 | 0.13 | 0.18 | 0.16 | 88.8 | 3 |
| Pb | mg/kg | F1 | | | 0.096 | | 0.060 | 0.096 | 0.099 | 0.030 | 30.7 | 6 |
| | mg/kg | F2 | | | 0.080 | | 0.072 | 0.077 | 0.080 | 0.015 | 18.9 | 5 |
| | mg/kg | F3 | | | 0.14 | | 0.16 | 0.14 | 0.14 | 0.02 | 15.1 | 5 |
| | mg/kg | F4 | | | 0.082 | | 0.095 | 0.084 | 0.082 | 0.012 | 14.9 | 5 |
| | mg/kg | F5 | | | 0.0095 | | 0.0110 | 0.0095 | 0.0090 | 0.0035 | 38.7 | 4 |
| | mg/kg | F6 | | | 0.016 | | 0.017 | 0.016 | 0.016 | 0.003 | 19.1 | 4 |
| | mg/kg | F7 | | | 0.024 | | *<0.019* | 0.024 | 0.024 | 0.008 | 33.8 | 3 |
| | mg/kg | LS_2lower | | | 0.39 | | 4.02 | 0.39 | 0.39 | 0.01 | 3.5 | 3 |
| | mg/kg | LS10lower | | | 0.43 | | 4.07 | 0.43 | 0.42 | 0.03 | 7.5 | 4 |
| | mg/kg | LS10upper | | | | | 4.11 | 2.32 | 2.32 | 2.54 | 109.5 | 2 |
| pH | | F1 | | 3.47 | 13.6 | 3.6 | 14.5 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F2 | | 3.33 | 13.7 | 3.6 | 14.5 | 13.6 | 13.7 | 0.2 | 1.4 | 4 |
| | | F3 | | 3.26 | 13.8 | 3.6 | 14.6 | 13.8 | 13.8 | 0.2 | 1.3 | 4 |
| | | F4 | | 3.32 | 13.3 | 3.8 | 14.1 | 13.3 | 13.2 | 0.2 | 1.5 | 4 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| pH | | F5 | | 1.16 | 12.8 | 3.9 | 13.1 | 12.8 | 12.8 | 0.2 | 1.4 | 6 |
| | | F6 | | 0.57 | 12.7 | 3.9 | 12.8 | 12.7 | 12.6 | 0.3 | 2.1 | 6 |
| | | F7 | | 0.52 | 12.7 | 3.9 | 12.8 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |
| Sb | mg/kg | F1 | | | 0.0035 | | *<0.005* | 0.0020 | 0.0035 | 0.0026 | 75.8 | 3 |
| | mg/kg | F2 | | | 0.0019 | | *<0.005* | 0.0020 | 0.0019 | 0.0005 | 24.1 | 3 |
| | mg/kg | F3 | | | 0.0087 | | *<0.005* | 0.0030 | 0.0087 | 0.0106 | 121.7 | 3 |
| | mg/kg | F4 | | | 0.0031 | | *<0.005* | 0.0010 | 0.0031 | 0.0036 | 117.3 | 3 |
| | mg/kg | F5 | | | | | *<0.005* | 0.0021 | 0.0021 | 0.0030 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.005* | 0.0046 | 0.0046 | 0.0065 | 141.4 | 2 |
| | mg/kg | F7 | | | | | *<0.005* | 0.0055 | 0.0055 | 0.0078 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | | | 0.0000 | 0.0033 | 0.0034 | 0.0039 | 115.6 | 4 |
| | mg/kg | LS_2upper | | | | | 0.048 | 0.048 | 0.068 | 0.074 | 108.1 | 3 |
| | mg/kg | LS10lower | | | | | 0.0000 | 0.0000 | 0.0023 | 0.0040 | 173.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.13 | 0.17 | 0.17 | 0.06 | 34.8 | 2 |
| Se | mg/kg | F1 | | | 0.049 | | 0.015 | 0.050 | 0.049 | 0.022 | 44.5 | 5 |
| | mg/kg | F2 | | | 0.025 | | 0.030 | 0.025 | 0.025 | 0.006 | 25.0 | 4 |
| | mg/kg | F3 | | | 0.032 | | 0.047 | 0.025 | 0.032 | 0.017 | 53.7 | 5 |
| | mg/kg | F4 | | | 0.0047 | | 0.0149 | 0.0047 | 0.0066 | 0.0060 | 91.5 | 4 |
| | mg/kg | F5 | | | | | *<0.005* | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | *<0.005* | | | | | |
| | mg/kg | F7 | | | | | *<0.005* | 0.002 | 0.002 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | 0.11 | | 1.22 | 0.12 | 0.11 | 0.02 | 19.6 | 3 |
| | mg/kg | LS_2upper | | | | | 1.23 | 0.20 | 0.20 | 0.11 | 53.7 | 2 |
| | mg/kg | LS10lower | | | 0.11 | | 1.22 | 0.12 | 0.11 | 0.02 | 18.5 | 3 |
| | mg/kg | LS10upper | | | | | 1.31 | 0.38 | 0.38 | 0.23 | 60.1 | 3 |
| $SO_4$ | mg/kg | F1 | | | 2350 | | 1521 | 2350 | 2332 | 660 | 28.3 | 6 |
| | mg/kg | F2 | | | 2300 | | 2248 | 2300 | 2444 | 565 | 23.1 | 5 |
| | mg/kg | F3 | | | 5990 | | 5191 | 5990 | 5718 | 895 | 15.6 | 5 |
| | mg/kg | F4 | | | 2813 | | 2813 | 2813 | 2273 | 1516 | 66.7 | 5 |
| | mg/kg | F5 | | | 6.96 | | 3.92 | 6.96 | 8.93 | 6.99 | 78.3 | 4 |
| | mg/kg | F6 | | | 4.93 | | 1.19 | 4.93 | 8.46 | 9.72 | 114.9 | 4 |
| | mg/kg | F7 | | | 7.31 | | 4.93 | 8.50 | 7.31 | 2.06 | 28.2 | 3 |
| | mg/kg | LS_2lower | | | 13206 | | 117276 | 14160 | 13206 | 1691 | 12.8 | 3 |
| | mg/kg | LS10lower | | | 13290 | | 117287 | 13290 | 13016 | 1442 | 11.1 | 4 |
| V | mg/kg | F1 | | | 0.13 | | 0.05 | 0.13 | 0.12 | 0.05 | 38.3 | 5 |
| | mg/kg | F2 | | | 0.10 | | 0.14 | 0.10 | 0.10 | 0.04 | 35.6 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.35 | 0.11 | 0.11 | 0.03 | 30.6 | 4 |
| | mg/kg | F4 | | | 0.020 | | 0.090 | 0.020 | 0.035 | 0.038 | 107.6 | 4 |
| | mg/kg | F5 | | | | | *<0.005* | | | | | |
| | mg/kg | F6 | | | | | *<0.005* | | | | | |
| | mg/kg | F7 | | | | | *<0.005* | | | | | |
| | mg/kg | LS_2lower | | | 0.36 | | 6.04 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| | mg/kg | LS_2upper | | | | | 6.05 | 0.48 | 2.33 | 3.22 | 138.2 | 3 |
| | mg/kg | LS10lower | | | 0.36 | | 6.04 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| | mg/kg | LS10upper | | | | | 6.13 | 0.56 | 2.39 | 3.24 | 135.3 | 3 |
| Zn | mg/kg | F1 | | | 94.0 | | 50.5 | 94.0 | 98.4 | 41.0 | 41.6 | 5 |
| | mg/kg | F2 | | | 79.8 | | 77.6 | 79.8 | 78.2 | 22.5 | 28.7 | 4 |
| | mg/kg | F3 | | | 106 | | 161 | 106 | 110 | 47 | 42.7 | 4 |

| Participant 5 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| Zn | mg/kg | F4 | | | 31.7 | | 61.0 | 31.7 | 33.8 | 23.8 | 70.4 | 4 |
| | mg/kg | F5 | | | 0.78 | | 0.89 | 0.78 | 0.99 | 0.87 | 87.6 | 4 |
| | mg/kg | F6 | | | 0.66 | | 1.24 | 0.66 | 0.73 | 0.44 | 59.9 | 4 |
| | mg/kg | F7 | | | 0.74 | | 0.99 | 0.74 | 0.74 | 0.31 | 41.3 | 4 |
| | mg/kg | LS_2lower | | | 260 | | 3741 | 260 | 260 | 82 | 31.5 | 2 |
| | mg/kg | LS10lower | | | 278 | | 3746 | 312 | 278 | 65 | 23.5 | 3 |

| Participant 6 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Measurand** | **Unit** | **Sample** | -3 0 3 | **z score** | **Assigned value** | **2×$s_{pt}$ %** | **Participant's result** | **Md** | **Mean** | **s** | **s %** | **$n_{stat}$** |
| As | mg/kg | F1 | | | 0.074 | | 0.052 | 0.074 | 0.074 | 0.035 | 47.2 | 6 |
| | mg/kg | LS10upper | | | | | *<0.0619* | 0.33 | 0.33 | 0.10 | 30.5 | 2 |
| Ba | mg/kg | F1 | | | 0.20 | | 0.23 | 0.20 | 0.21 | 0.11 | 54.2 | 6 |
| | mg/kg | LS10lower | | | 496 | | 19 | 468 | 496 | 88 | 17.7 | 3 |
| Cd | mg/kg | F1 | | | | | *<0.00150* | 0.0004 | 0.0003 | 0.0001 | 42.7 | 3 |
| | mg/kg | LS10upper | | | | | *<0.00299* | 0.054 | 0.066 | 0.069 | 105.4 | 3 |
| Cl | mg/kg | F1 | | | 756 | | 450 | 756 | 675 | 298 | 44.1 | 6 |
| | mg/kg | LS10lower | | | 1606 | | 1640 | 1606 | 1573 | 163 | 10.4 | 4 |
| Conductivity | mS/m | F1 | | | 33265 | | *>11200* | 33265 | 32950 | 2642 | 8.0 | 4 |
| | mS/m | F7 | | | 753 | | 4680 | 966 | 753 | 410 | 54.5 | 5 |
| Cr | mg/kg | F1 | | | 0.41 | | 0.68 | 0.41 | 0.43 | 0.20 | 47.6 | 6 |
| | mg/kg | LS10lower | | | 1.08 | | 2.76 | 1.08 | 1.35 | 1.00 | 74.2 | 4 |
| Cu | mg/kg | F1 | | | 0.11 | | 0.09 | 0.11 | 0.13 | 0.07 | 54.7 | 6 |
| | mg/kg | LS10lower | | | 0.23 | | 0.20 | 0.23 | 0.28 | 0.15 | 53.0 | 4 |
| DOC | mg/kg | F1 | | | 420 | | 170 | 420 | 475 | 375 | 78.9 | 4 |
| | mg/kg | LS10lower | | | 4309 | | 625 | 3187 | 4309 | 4355 | 101.1 | 3 |
| F | mg/kg | F1 | | | 3.92 | | 0.52 | 3.92 | 6.09 | 6.90 | 113.2 | 4 |
| | mg/kg | LS10lower | | | 7.96 | | 11.40 | 6.90 | 7.96 | 3.05 | 38.3 | 3 |
| Hg | mg/kg | F1 | | | | | *<0.00100* | 0.0001 | 0.0017 | 0.0028 | 168.4 | 3 |
| | mg/kg | LS10upper | | | | | *<0.00199* | 0.17 | 0.17 | 0.18 | 111.5 | 2 |
| Mo | mg/kg | F1 | | | 0.33 | | 0.19 | 0.33 | 0.30 | 0.11 | 38.6 | 6 |
| | mg/kg | LS10lower | | | 0.99 | | 0.96 | 0.99 | 1.00 | 0.05 | 5.0 | 4 |
| Ni | mg/kg | F1 | | | | | *<0.0250* | 0.0022 | 0.0018 | 0.0007 | 38.5 | 3 |
| | mg/kg | LS10upper | | | | | 0.05 | 0.13 | 0.18 | 0.16 | 88.8 | 3 |
| Pb | mg/kg | F1 | | | 0.096 | | 0.110 | 0.096 | 0.099 | 0.030 | 30.7 | 6 |
| | mg/kg | LS10lower | | | 0.43 | | 0.43 | 0.43 | 0.42 | 0.03 | 7.5 | 4 |
| pH | | F1 | | -1.23 | 13.6 | 3.6 | 13.3 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F7 | | 0.81 | 12.7 | 3.9 | 12.9 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |
| Sb | mg/kg | F1 | | | 0.0035 | | *<0.0100* | 0.0020 | 0.0035 | 0.0026 | 75.8 | 3 |
| | mg/kg | LS10upper | | | | | *<0.0199* | 0.17 | 0.17 | 0.06 | 34.8 | 2 |
| Se | mg/kg | F1 | | | 0.049 | | *<0.500* | 0.050 | 0.049 | 0.022 | 44.5 | 5 |
| | mg/kg | LS10upper | | | | | 0.62 | 0.38 | 0.38 | 0.23 | 60.1 | 3 |
| $SO_4$ | mg/kg | F1 | | | 2350 | | 2500 | 2350 | 2332 | 660 | 28.3 | 6 |
| | mg/kg | LS10lower | | | 13290 | | 12400 | 13290 | 13016 | 1442 | 11.1 | 4 |
| Zn | mg/kg | F1 | | | 94.0 | | 94.0 | 94.0 | 98.4 | 41.0 | 41.6 | 5 |
| | mg/kg | LS10lower | | | 278 | | 312 | 312 | 278 | 65 | 23.5 | 3 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| As | mg/kg | F1 | | | 0.074 | | 0.056 | 0.074 | 0.074 | 0.035 | 47.2 | 6 |
| | mg/kg | F2 | | | 0.050 | | 0.026 | 0.050 | 0.047 | 0.015 | 32.1 | 5 |
| | mg/kg | F3 | | | 0.051 | | 0.034 | 0.051 | 0.055 | 0.031 | 57.5 | 5 |
| | mg/kg | F4 | | | 0.0097 | | 0.0030 | 0.0059 | 0.0097 | 0.0097 | 99.8 | 4 |
| | mg/kg | F5 | | | | | 0.0000 | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0.0000 | 0.0005 | 0.0005 | 0.0006 | 141.4 | 2 |
| | mg/kg | F7 | | | | | 0.0000 | 0.0006 | 0.0006 | 0.0008 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | 0.19 | | 0.12 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| | mg/kg | LS10lower | | | 0.19 | | 0.12 | 0.20 | 0.19 | 0.07 | 34.7 | 3 |
| Ba | mg/kg | F1 | | | 0.20 | | 0.27 | 0.20 | 0.21 | 0.11 | 54.2 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.32 | 0.17 | 0.19 | 0.13 | 67.2 | 5 |
| | mg/kg | F3 | | | 0.83 | | 0.83 | 0.83 | 0.91 | 0.22 | 24.7 | 5 |
| | mg/kg | F4 | | | 1.27 | | 2.66 | 1.27 | 1.84 | 1.12 | 60.8 | 5 |
| | mg/kg | F5 | | | 37.3 | | 97.8 | 37.3 | 49.0 | 38.9 | 79.4 | 5 |
| | mg/kg | F6 | | | 209 | | 280 | 209 | 220 | 77 | 35.2 | 5 |
| | mg/kg | F7 | | | 208 | | 212 | 208 | 212 | 18 | 8.6 | 5 |
| | mg/kg | LS_2lower | | | 40.0 | | 101.9 | 40.0 | 53.4 | 43.3 | 81.1 | 3 |
| | mg/kg | LS10lower | | | 496 | | 594 | 468 | 496 | 88 | 17.7 | 3 |
| Cd | mg/kg | F1 | | | | | 0.0004 | 0.0004 | 0.0003 | 0.0001 | 42.7 | 3 |
| | mg/kg | F2 | | | | | 0.0010 | 0.0002 | 0.0005 | 0.0005 | 98.9 | 3 |
| | mg/kg | F3 | | | | | 0.0012 | 0.0004 | 0.0006 | 0.0005 | 86.8 | 3 |
| | mg/kg | F4 | | | | | 0.0005 | 0.0005 | 0.0005 | 0.0000 | 0.0 | 1 |
| | mg/kg | F5 | | | | | 0 | | | | | |
| | mg/kg | F6 | | | | | 0 | | | | | |
| | mg/kg | F7 | | | | | 0 | | | | | |
| | mg/kg | LS_2lower | | | | | 0.0004 | 0.0004 | 0.0051 | 0.0086 | 167.3 | 3 |
| | mg/kg | LS_2upper | | | | | 0.003 | 0.023 | 0.042 | 0.051 | 121.8 | 3 |
| | mg/kg | LS10lower | | | | | 0.0004 | 0.0004 | 0.0051 | 0.0086 | 167.2 | 3 |
| | mg/kg | LS10upper | | | | | 0.003 | 0.054 | 0.066 | 0.069 | 105.4 | 3 |
| Cl | mg/kg | F1 | | | 756 | | 780 | 756 | 675 | 298 | 44.1 | 6 |
| | mg/kg | F2 | | | 414 | | 280 | 414 | 382 | 71 | 18.7 | 5 |
| | mg/kg | F3 | | | 207 | | 201 | 207 | 227 | 93 | 40.9 | 4 |
| | mg/kg | F4 | | | 72.7 | | 31.5 | 51.0 | 72.7 | 40.7 | 56.0 | 5 |
| | mg/kg | F5 | | | 11.7 | | 10.0 | 10.0 | 11.7 | 3.3 | 28.3 | 5 |
| | mg/kg | F6 | | | 24.4 | | 26.4 | 22.5 | 24.4 | 5.0 | 20.3 | 5 |
| | mg/kg | F7 | | | 26.7 | | 19.5 | 23.6 | 26.7 | 9.5 | 35.6 | 4 |
| | mg/kg | LS_2lower | | | 1512 | | 1303 | 1552 | 1512 | 192 | 12.7 | 3 |
| | mg/kg | LS10lower | | | 1606 | | 1348 | 1606 | 1573 | 163 | 10.4 | 4 |
| Conductivity | mS/m | F1 | | | 33265 | | 34200 | 33265 | 32950 | 2642 | 8.0 | 4 |
| | mS/m | F2 | | | 34800 | | 34900 | 34800 | 33653 | 3251 | 9.7 | 4 |
| | mS/m | F3 | | | 32600 | | 33000 | 32600 | 32498 | 3053 | 9.4 | 4 |
| | mS/m | F4 | | | 15600 | | 11590 | 15600 | 16582 | 5073 | 30.6 | 5 |
| | mS/m | F5 | | | 1970 | | 1399 | 1970 | 1912 | 796 | 41.7 | 5 |
| | mS/m | F6 | | | 1122 | | 1115 | 1122 | 1119 | 46 | 4.1 | 4 |
| | mS/m | F7 | | | 753 | | 1064 | 966 | 753 | 410 | 54.5 | 5 |
| Cr | mg/kg | F1 | | | 0.41 | | 0.24 | 0.41 | 0.43 | 0.20 | 47.6 | 6 |
| | mg/kg | F2 | | | 0.17 | | 0.08 | 0.17 | 0.19 | 0.09 | 50.6 | 5 |
| | mg/kg | F3 | | | 0.26 | | 0.13 | 0.26 | 0.24 | 0.06 | 26.9 | 5 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Cr | mg/kg | F4 | | | 0.075 | | 0.021 | 0.091 | 0.075 | 0.045 | 60.8 | 5 |
| | mg/kg | F5 | | | | | 0.0010 | 0.0007 | 0.0007 | 0.0003 | 42.3 | 3 |
| | mg/kg | F6 | | | | | 0.0010 | 0.0006 | 0.0006 | 0.0006 | 94.3 | 2 |
| | mg/kg | F7 | | | | | 0.003 | | | | | |
| | mg/kg | LS_2lower | | | 0.84 | | 0.48 | 0.84 | 0.88 | 0.42 | 47.7 | 3 |
| | mg/kg | LS10lower | | | 1.08 | | 0.48 | 1.08 | 1.35 | 1.00 | 74.2 | 4 |
| Cu | mg/kg | F1 | | | 0.11 | | 0.06 | 0.11 | 0.13 | 0.07 | 54.7 | 6 |
| | mg/kg | F2 | | | 0.088 | | 0.031 | 0.088 | 0.092 | 0.041 | 44.4 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.05 | 0.11 | 0.13 | 0.08 | 61.6 | 5 |
| | mg/kg | F4 | | | 0.042 | | 0.016 | 0.042 | 0.048 | 0.031 | 65.8 | 4 |
| | mg/kg | F5 | | | 0.0082 | | 0.0010 | 0.0093 | 0.0082 | 0.0068 | 82.1 | 3 |
| | mg/kg | F6 | | | 0.032 | | 0.002 | 0.046 | 0.032 | 0.026 | 81.4 | 3 |
| | mg/kg | F7 | | | 0.033 | | 0.002 | 0.043 | 0.033 | 0.027 | 82.7 | 3 |
| | mg/kg | LS_2lower | | | 0.26 | | 0.16 | 0.26 | 0.28 | 0.12 | 43.9 | 3 |
| | mg/kg | LS10lower | | | 0.23 | | 0.17 | 0.23 | 0.28 | 0.15 | 53.0 | 4 |
| DOC | mg/kg | F1 | | | 420 | | 670 | 420 | 475 | 375 | 78.9 | 4 |
| | mg/kg | F2 | | | 396 | | 540 | 480 | 396 | 200 | 50.5 | 3 |
| | mg/kg | F3 | | | 926 | | 1440 | 1003 | 926 | 557 | 60.2 | 3 |
| | mg/kg | F4 | | | 279 | | 480 | 297 | 279 | 211 | 75.9 | 3 |
| | mg/kg | F5 | | | 18.8 | | 9.5 | 22.9 | 18.8 | 8.1 | 42.9 | 3 |
| | mg/kg | F6 | | | 41.0 | | 15.6 | 43.0 | 41.0 | 24.4 | 59.6 | 3 |
| | mg/kg | F7 | | | 62.0 | | 31.5 | 57.0 | 62.0 | 33.3 | 53.7 | 3 |
| | mg/kg | LS_2lower | | | | | 3140 | 5964 | 5964 | 3995 | 67.0 | 2 |
| | mg/kg | LS10lower | | | 4309 | | 3187 | 3187 | 4309 | 4355 | 101.1 | 3 |
| F | mg/kg | F1 | | | 3.92 | | 2.50 | 3.92 | 6.09 | 6.90 | 113.2 | 4 |
| | mg/kg | F2 | | | 6.04 | | 1.70 | 6.41 | 6.04 | 4.16 | 69.0 | 3 |
| | mg/kg | F3 | | | 7.25 | | 3.00 | 7.25 | 7.73 | 5.89 | 76.2 | 4 |
| | mg/kg | F4 | | | 2.58 | | 0.90 | 2.58 | 2.63 | 1.54 | 58.3 | 4 |
| | mg/kg | F5 | | | 0.58 | | 0.22 | 0.58 | 0.58 | 0.51 | 87.9 | 2 |
| | mg/kg | F6 | | | | | 0.63 | | | | | |
| | mg/kg | F7 | | | | | 0.95 | | | | | |
| | mg/kg | LS_2lower | | | 5.45 | | 5.32 | 5.45 | 5.45 | 0.18 | 3.4 | 2 |
| | mg/kg | LS_2upper | | | | | 8.32 | 9.96 | 9.96 | 2.32 | 23.3 | 2 |
| | mg/kg | LS10lower | | | 7.96 | | 6.90 | 6.90 | 7.96 | 3.05 | 38.3 | 3 |
| | mg/kg | LS10upper | | | | | 9.9 | 12.8 | 12.8 | 4.0 | 31.6 | 2 |
| Hg | mg/kg | F1 | | | | | 0.0000 | 0.0001 | 0.0017 | 0.0028 | 168.4 | 3 |
| | mg/kg | F2 | | | | | 0.0000 | 0.0001 | 0.0018 | 0.0031 | 170.3 | 3 |
| | mg/kg | F3 | | | | | 0.0000 | 0.0001 | 0.0028 | 0.0048 | 169.3 | 3 |
| | mg/kg | F4 | | | | | 0.0000 | 0.0000 | 0.0010 | 0.0018 | 170.6 | 3 |
| | mg/kg | F5 | | | | | 0 | | | | | |
| | mg/kg | F6 | | | | | 0 | | | | | |
| | mg/kg | F7 | | | | | 0 | | | | | |
| | mg/kg | LS_2lower | | | | | 0.000 | 0.000 | 0.093 | 0.161 | 173.2 | 3 |
| | mg/kg | LS10lower | | | | | 0.000 | 0.000 | 0.093 | 0.161 | 173.2 | 3 |
| Mo | mg/kg | F1 | | | 0.33 | | 0.38 | 0.33 | 0.30 | 0.11 | 38.6 | 6 |
| | mg/kg | F2 | | | 0.23 | | 0.21 | 0.23 | 0.25 | 0.03 | 13.7 | 5 |
| | mg/kg | F3 | | | 0.28 | | 0.32 | 0.28 | 0.28 | 0.03 | 10.6 | 4 |
| | mg/kg | F4 | | | 0.099 | | 0.045 | 0.093 | 0.099 | 0.044 | 44.7 | 5 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | 2×$s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| Mo | mg/kg | F5 | | | 0.0031 | | 0.0010 | 0.0034 | 0.0031 | 0.0020 | 63.5 | 3 |
| | mg/kg | F6 | | | 0.0031 | | 0.0030 | 0.0031 | 0.0031 | 0.0001 | 4.6 | 2 |
| | mg/kg | F7 | | | 0.0040 | | 0.0040 | 0.0040 | 0.0040 | 0.0000 | 0.0 | 2 |
| | mg/kg | LS_2lower | | | 1.01 | | 0.96 | 1.01 | 1.01 | 0.06 | 5.4 | 3 |
| | mg/kg | LS10lower | | | 0.99 | | 0.97 | 0.99 | 1.00 | 0.05 | 5.0 | 4 |
| Ni | mg/kg | F1 | | | | | 0.0010 | 0.0022 | 0.0018 | 0.0007 | 38.5 | 3 |
| | mg/kg | F2 | | | | | 0.0000 | 0.0011 | 0.0008 | 0.0007 | 87.5 | 3 |
| | mg/kg | F3 | | | | | 0.0010 | 0.0010 | 0.0009 | 0.0001 | 12.4 | 3 |
| | mg/kg | F4 | | | | | 0.0000 | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F5 | | | | | 0.0000 | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0.0000 | 0.0002 | 0.0002 | 0.0002 | 141.4 | 2 |
| | mg/kg | F7 | | | | | 0.001 | 0.001 | 0.001 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | | | 0.0030 | 0.0015 | 0.0019 | 0.0022 | 120.0 | 4 |
| | mg/kg | LS10lower | | | | | 0.003 | 0.000 | 0.001 | 0.002 | 173.2 | 3 |
| Pb | mg/kg | F1 | | | 0.096 | | 0.093 | 0.096 | 0.099 | 0.030 | 30.7 | 6 |
| | mg/kg | F2 | | | 0.080 | | 0.079 | 0.077 | 0.080 | 0.015 | 18.9 | 5 |
| | mg/kg | F3 | | | 0.14 | | 0.14 | 0.14 | 0.14 | 0.02 | 15.1 | 5 |
| | mg/kg | F4 | | | 0.082 | | 0.062 | 0.084 | 0.082 | 0.012 | 14.9 | 5 |
| | mg/kg | F5 | | | 0.0095 | | 0.0080 | 0.0095 | 0.0090 | 0.0035 | 38.7 | 4 |
| | mg/kg | F6 | | | 0.016 | | 0.020 | 0.016 | 0.016 | 0.003 | 19.1 | 4 |
| | mg/kg | F7 | | | 0.024 | | 0.032 | 0.024 | 0.024 | 0.008 | 33.8 | 3 |
| | mg/kg | LS_2lower | | | 0.39 | | 0.39 | 0.39 | 0.39 | 0.01 | 3.5 | 3 |
| | mg/kg | LS10lower | | | 0.43 | | 0.44 | 0.43 | 0.42 | 0.03 | 7.5 | 4 |
| pH | | F1 | | -0.29 | 13.6 | 3.6 | 13.5 | 13.7 | 13.6 | 0.3 | 1.9 | 5 |
| | | F2 | | -0.36 | 13.7 | 3.6 | 13.6 | 13.6 | 13.7 | 0.2 | 1.4 | 4 |
| | | F3 | | -0.97 | 13.8 | 3.6 | 13.6 | 13.8 | 13.8 | 0.2 | 1.3 | 4 |
| | | F4 | | -0.51 | 13.3 | 3.8 | 13.2 | 13.3 | 13.2 | 0.2 | 1.5 | 4 |
| | | F5 | | -0.20 | 12.8 | 3.9 | 12.8 | 12.8 | 12.8 | 0.2 | 1.4 | 6 |
| | | F6 | | -0.28 | 12.7 | 3.9 | 12.6 | 12.7 | 12.6 | 0.3 | 2.1 | 6 |
| | | F7 | | -0.16 | 12.7 | 3.9 | 12.7 | 12.8 | 12.7 | 0.3 | 2.1 | 7 |
| Sb | mg/kg | F1 | | | 0.0035 | | 0.0020 | 0.0020 | 0.0035 | 0.0026 | 75.8 | 3 |
| | mg/kg | F2 | | | 0.0019 | | 0.0020 | 0.0020 | 0.0019 | 0.0005 | 24.1 | 3 |
| | mg/kg | F3 | | | 0.0087 | | 0.0030 | 0.0030 | 0.0087 | 0.0106 | 121.7 | 3 |
| | mg/kg | F4 | | | 0.0031 | | 0.0010 | 0.0010 | 0.0031 | 0.0036 | 117.3 | 3 |
| | mg/kg | F5 | | | | | 0.0000 | 0.0021 | 0.0021 | 0.0030 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0.0000 | 0.0046 | 0.0046 | 0.0065 | 141.4 | 2 |
| | mg/kg | F7 | | | | | 0.0000 | 0.0055 | 0.0055 | 0.0078 | 141.4 | 2 |
| | mg/kg | LS_2lower | | | | | 0.0070 | 0.0033 | 0.0034 | 0.0039 | 115.6 | 4 |
| | mg/kg | LS10lower | | | | | 0.0070 | 0.0000 | 0.0023 | 0.0040 | 173.2 | 3 |
| Se | mg/kg | F1 | | | 0.049 | | 0.046 | 0.050 | 0.049 | 0.022 | 44.5 | 5 |
| | mg/kg | F2 | | | 0.025 | | 0.019 | 0.025 | 0.025 | 0.006 | 25.0 | 4 |
| | mg/kg | F3 | | | 0.032 | | 0.020 | 0.025 | 0.032 | 0.017 | 53.7 | 5 |
| | mg/kg | F4 | | | 0.0047 | | 0.0020 | 0.0047 | 0.0066 | 0.0060 | 91.5 | 4 |
| | mg/kg | F5 | | | | | 0.0000 | 0.0001 | 0.0001 | 0.0001 | 141.4 | 2 |
| | mg/kg | F6 | | | | | 0 | | | | | |
| | mg/kg | F7 | | | | | 0.002 | 0.002 | 0.002 | 0.000 | 0.0 | 1 |
| | mg/kg | LS_2lower | | | 0.11 | | 0.09 | 0.12 | 0.11 | 0.02 | 19.6 | 3 |
| | mg/kg | LS10lower | | | 0.11 | | 0.09 | 0.12 | 0.11 | 0.02 | 18.5 | 3 |

| Participant 8 | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Measurand | Unit | Sample | -3 0 3 | z score | Assigned value | $2 \times s_{pt}$ % | Participant's result | Md | Mean | s | s % | $n_{stat}$ |
| $SO_4$ | mg/kg | F1 | | | 2350 | | 3000 | 2350 | 2332 | 660 | 28.3 | 6 |
| | mg/kg | F2 | | | 2300 | | 3000 | 2300 | 2444 | 565 | 23.1 | 5 |
| | mg/kg | F3 | | | 5990 | | 4500 | 5990 | 5718 | 895 | 15.6 | 5 |
| | mg/kg | F4 | | | 2813 | | 750 | 2813 | 2273 | 1516 | 66.7 | 5 |
| | mg/kg | F5 | | | 6.96 | | 3.40 | 6.96 | 8.93 | 6.99 | 78.3 | 4 |
| | mg/kg | F6 | | | 4.93 | | 5.10 | 4.93 | 8.46 | 9.72 | 114.9 | 4 |
| | mg/kg | F7 | | | 7.31 | | 8.50 | 8.50 | 7.31 | 2.06 | 28.2 | 3 |
| | mg/kg | LS_2lower | | | 13206 | | 11253 | 14160 | 13206 | 1691 | 12.8 | 3 |
| | mg/kg | LS10lower | | | 13290 | | 11267 | 13290 | 13016 | 1442 | 11.1 | 4 |
| V | mg/kg | F1 | | | 0.13 | | 0.13 | 0.13 | 0.12 | 0.05 | 38.3 | 5 |
| | mg/kg | F2 | | | 0.10 | | 0.08 | 0.10 | 0.10 | 0.04 | 35.6 | 5 |
| | mg/kg | F3 | | | 0.11 | | 0.11 | 0.11 | 0.11 | 0.03 | 30.6 | 4 |
| | mg/kg | F4 | | | 0.020 | | 0.011 | 0.020 | 0.035 | 0.038 | 107.6 | 4 |
| | mg/kg | F5 | | | | | 0 | | | | | |
| | mg/kg | F6 | | | | | 0 | | | | | |
| | mg/kg | F7 | | | | | 0 | | | | | |
| | mg/kg | LS_2lower | | | 0.36 | | 0.33 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| | mg/kg | LS10lower | | | 0.36 | | 0.33 | 0.36 | 0.39 | 0.08 | 20.6 | 3 |
| Zn | mg/kg | F1 | | | 94.0 | | 75.5 | 94.0 | 98.4 | 41.0 | 41.6 | 5 |
| | mg/kg | F2 | | | 79.8 | | 49.3 | 79.8 | 78.2 | 22.5 | 28.7 | 4 |
| | mg/kg | F3 | | | 106 | | 66 | 106 | 110 | 47 | 42.7 | 4 |
| | mg/kg | F4 | | | 31.7 | | 10.9 | 31.7 | 33.8 | 23.8 | 70.4 | 4 |
| | mg/kg | F5 | | | 0.78 | | 0.19 | 0.78 | 0.99 | 0.87 | 87.6 | 4 |
| | mg/kg | F6 | | | 0.66 | | 0.39 | 0.66 | 0.73 | 0.44 | 59.9 | 4 |
| | mg/kg | F7 | | | 0.74 | | 0.50 | 0.74 | 0.74 | 0.31 | 41.3 | 4 |
| | mg/kg | LS_2lower | | | 260 | | 202 | 260 | 260 | 82 | 31.5 | 2 |
| | mg/kg | LS10lower | | | 278 | | 203 | 312 | 278 | 65 | 23.5 | 3 |

## Appendix 7.Summary of the $E_n$ scores

| Measurand | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | % |
|---|---|---|---|---|---|---|---|---|---|---|
| As | F1 | | 0.5 | | | -1.6 | -0.7 | | -0.5 | 75.0 |
| | F2 | | 0.1 | | | 0.0 | | | -1.4 | 66.7 |
| | F3 | | 0.1 | | | 1.9 | | | -0.6 | 66.7 |
| | LS_2lower | | | | | 7.2 | | | -0.8 | 50.0 |
| | LS10lower | | | | | 7.2 | | | -0.8 | 50.0 |
| Ba | F1 | | -0.5 | | | -0.2 | 0.3 | | 0.5 | 100 |
| | F3 | | -0.2 | | | 1.7 | | | 0.0 | 66.7 |
| | F4 | | -0.4 | | | 0.0 | | | 1.1 | 66.7 |
| | F6 | | 0.0 | | | 1.3 | | | 0.5 | 66.7 |
| | F7 | | 0.5 | | | 0.0 | | | 0.1 | 100 |
| | LS10lower | | | | | 4.0 | -4.7 | | 0.4 | 33.3 |
| Cl | F1 | | -0.1 | | | -2.0 | -1.1 | | 0.1 | 50.0 |
| | F2 | | 0.3 | | | 0.0 | | | -1.0 | 66.7 |
| | F3 | | 1.2 | | | 5.0 | | | -0.1 | 33.3 |
| | F4 | | 1.0 | | | 1.1 | | | -1.1 | 0 |
| | F5 | | 1.1 | | | -0.6 | | | -0.3 | 66.7 |
| | F6 | | -0.3 | | | -0.4 | | | 0.2 | 100 |
| | F7 | | -0.6 | | | 0.0 | | | -0.6 | 100 |
| | LS_2lower | | | | | 9.0 | | | -0.5 | 50.0 |
| | LS10lower | | | | | 9.0 | 0.1 | | -0.6 | 66.7 |
| Conductivity | F1 | | -0.9 | | | | | | 0.2 | 100 |
| | F2 | | -1.3 | | | | | | 0.0 | 50.0 |
| | F3 | | -0.9 | | | | | | 0.1 | 100 |
| | F4 | | 1.1 | | | | | | -0.9 | 50.0 |
| | F5 | | 1.4 | | | | | | -0.8 | 50.0 |
| | F6 | | 0.0 | | | | | | -0.1 | 100 |
| | F7 | | 0.8 | | | | 3.6 | | 0.8 | 66.7 |
| Cr | F1 | | 0.7 | | | -1.2 | 1.2 | | -0.9 | 50.0 |
| | F2 | | 1.1 | | | -0.2 | | | -1.1 | 33.3 |
| | F3 | | 0.0 | | | 0.4 | | | -1.5 | 66.7 |
| | F4 | | 0.5 | | | 1.1 | | | -1.3 | 33.3 |
| | LS_2lower | | | | | 6.4 | | | -0.7 | 50.0 |
| | LS10lower | | | | | 5.7 | 1.7 | | -0.7 | 33.3 |
| Cu | F1 | | 0.1 | | | 0.0 | -0.4 | | -0.9 | 100 |
| | F2 | | -0.1 | | | 1.3 | | | -1.5 | 33.3 |
| | F3 | | -0.7 | | | 2.0 | | | -0.9 | 66.7 |
| | F4 | | | | | 1.6 | | | -0.9 | 50.0 |
| | LS_2lower | | | | | 7.3 | | | -0.7 | 50.0 |
| | LS10lower | | | | | 7.3 | -0.2 | | -0.5 | 66.7 |
| DOC | F2 | | | | | | | | 0.5 | 100 |
| | F3 | | | | | | | | 0.6 | 100 |
| | F5 | | | | | | | | -0.9 | 100 |
| | F6 | | | | | | | | -0.9 | 100 |
| | F7 | | | | | | | | -0.8 | 100 |
| F | F2 | | | | | 0.1 | | | -0.9 | 100 |
| | F4 | | 0.3 | | | 1.1 | | | -1.1 | 33.3 |
| | LS10lower | | | | | 6.5 | 0.8 | | -0.3 | 66.7 |

| Measurand | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | % |
|---|---|---|---|---|---|---|---|---|---|---|
| Mo | F1 | . | 0.5 | . | . | -1.8 | -1.2 | . | 0.3 | 50.0 |
| | F2 | . | 0.0 | . | . | 0.9 | . | . | -0.2 | 100 |
| | F3 | . | -0.1 | . | . | 2.9 | . | . | 0.3 | 66.7 |
| | F4 | . | 0.8 | . | . | 0.9 | . | . | -1.2 | 66.7 |
| | LS_2lower | . | . | . | . | 6.3 | . | . | -0.1 | 50.0 |
| | LS10lower | . | . | . | . | 6.3 | -0.1 | . | -0.1 | 66.7 |
| Pb | F1 | . | 0.1 | . | . | -1.4 | 0.4 | . | -0.1 | 75.0 |
| | F2 | . | -0.5 | . | . | -0.5 | . | . | 0.0 | 100 |
| | F3 | . | -0.5 | . | . | 0.6 | . | . | 0.1 | 100 |
| | F4 | . | 0.2 | . | . | 0.7 | . | . | -0.7 | 100 |
| | F5 | . | . | . | . | 0.4 | . | . | -0.3 | 100 |
| | F6 | . | . | . | . | 0.2 | . | . | 0.5 | 100 |
| | F7 | . | . | . | . | . | . | . | 0.5 | 100 |
| | LS_2lower | . | . | . | . | 5.9 | . | . | 0.0 | 50.0 |
| | LS10lower | . | . | . | . | 5.8 | 0.0 | . | 0.0 | 66.7 |
| pH | F1 | . | 0.5 | . | . | . | -0.1 | . | -0.3 | 100 |
| | F2 | . | 0.4 | . | . | . | . | . | -0.5 | 100 |
| | F3 | . | 0.3 | . | . | . | . | . | -1.3 | 50.0 |
| | F4 | . | -0.4 | . | . | . | . | . | -0.6 | 100 |
| | F5 | . | 0.3 | . | . | . | . | . | -0.3 | 100 |
| | F6 | . | 0.4 | . | . | . | . | . | -0.3 | 100 |
| | F7 | . | 0.4 | . | . | . | 0.1 | . | -0.2 | 100 |
| Sb | F2 | . | . | . | . | . | . | . | 0.1 | 100 |
| Se | F1 | . | 0.9 | . | . | -1.7 | . | . | -0.1 | 66.7 |
| | F2 | . | . | . | . | 0.4 | . | . | -0.6 | 100 |
| | F3 | . | 0.9 | . | . | 0.7 | . | . | -0.7 | 100 |
| | LS_2lower | . | . | . | . | 2.8 | . | . | -0.5 | 50.0 |
| | LS10lower | . | . | . | . | 2.8 | . | . | -0.5 | 50.0 |
| $SO_4$ | F1 | . | -0.2 | . | . | -1.5 | 0.2 | . | 0.5 | 75.0 |
| | F2 | . | 0.0 | . | . | -0.1 | . | . | 0.5 | 100 |
| | F3 | . | 0.1 | . | . | -0.8 | . | . | -0.8 | 100 |
| | F7 | . | 0.4 | . | . | -1.0 | . | . | 0.3 | 100 |
| | LS_2lower | . | . | . | . | 8.8 | . | . | -0.5 | 50.0 |
| | LS10lower | . | . | . | . | 8.8 | -0.3 | . | -0.5 | 66.7 |
| V | F1 | . | 0.4 | . | . | -1.7 | . | . | -0.1 | 66.7 |
| | F2 | . | 0.0 | . | . | 1.0 | . | . | -0.5 | 100 |
| | F3 | . | -0.2 | . | . | 3.6 | . | . | 0.1 | 66.7 |
| | LS_2lower | . | . | . | . | 5.7 | . | . | -0.2 | 50.0 |
| | LS10lower | . | . | . | . | 5.7 | . | . | -0.2 | 50.0 |
| Zn | F1 | . | 0.4 | . | . | -1.2 | 0.0 | . | -0.4 | 75.0 |
| | F2 | . | 0.1 | . | . | -0.1 | . | . | -1.0 | 66.7 |
| | F3 | . | -0.6 | . | . | 1.1 | . | . | -0.8 | 66.7 |
| | F6 | . | 0.6 | . | . | 1.4 | . | . | -0.6 | 66.7 |
| | F7 | . | 0.6 | . | . | 0.8 | . | . | -0.7 | 100 |
| | LS10lower | . | . | . | . | 7.4 | 0.3 | . | -0.7 | 66.7 |
| % | | | 88 | | | 38 | 71 | | 87 | |

$-1.0 \leq E_n \leq 1.0$ – satisfactory  $E_n > 1.0$ or $E_n < -1.0$ – unsatisfactory  % - percentage of satisfactory results

Totally satisfactory, % in all: 72

## Appendix 8. Summary of the D% scores

| Measurand | Unit | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| As | mg/kg | F1 | 64.9 | **24.2** | 30.7 | . | -63.5 | -29.7 | **-24.3** |
| | mg/kg | F2 | 34.0 | **4.6** | **-18.8** | . | **0.0** | . | -48.0 |
| | mg/kg | F3 | **0.0** | **4.3** | -46.3 | . | 109.8 | . | -33.3 |
| | mg/kg | F4 | -26.8 | . | -51.5 | . | 147.4 | . | -69.1 |
| | mg/kg | LS_2lower | 30.0 | **3.7** | . | . | 1073.2 | . | -37.9 |
| | mg/kg | LS10lower | 30.0 | **3.7** | . | . | 1073.2 | . | -37.9 |
| Ba | mg/kg | F1 | 86.5 | -26.5 | -78.0 | . | **-10.5** | **15.0** | 35.0 |
| | mg/kg | F2 | 97.6 | -38.2 | -75.5 | . | **-1.8** | . | 88.2 |
| | mg/kg | F3 | **22.9** | **-6.6** | **-19.1** | . | 49.2 | . | **0.0** |
| | mg/kg | F4 | -27.0 | **-24.3** | 167.5 | . | **0.2** | . | 109.4 |
| | mg/kg | F5 | **0.0** | -56.0 | 118.8 | . | -68.8 | . | 162.3 |
| | mg/kg | F6 | **-7.2** | **0.0** | -47.7 | . | 46.2 | . | 33.8 |
| | mg/kg | F7 | **-8.2** | **15.9** | **-0.8** | . | **0.0** | . | **2.1** |
| | mg/kg | LS_2lower | **0.0** | -54.0 | . | . | **9.6** | . | 154.8 |
| | mg/kg | LS10lower | **-14.3** | **-5.6** | . | . | 139.8 | -96.2 | **19.7** |
| Cl | mg/kg | F1 | **14.8** | **-3.3** | 34.7 | . | -73.2 | -40.5 | **3.2** |
| | mg/kg | F2 | **0.0** | **10.9** | **-17.9** | . | **0.7** | . | -32.4 |
| | mg/kg | F3 | **2.9** | 72.5 | -33.8 | . | 281.9 | . | **-2.9** |
| | mg/kg | F4 | -34.0 | 65.1 | -29.8 | . | 55.3 | . | -56.7 |
| | mg/kg | F5 | **-20.5** | 47.9 | **2.6** | . | **-16.3** | . | **-14.5** |
| | mg/kg | F6 | **-22.1** | **-8.6** | 31.1 | . | **-7.7** | . | **8.2** |
| | mg/kg | F7 | . | **-24.3** | 49.8 | . | **1.5** | . | -27.0 |
| | mg/kg | LS_2lower | **2.6** | **11.1** | . | . | 1032.3 | . | **-13.9** |
| | mg/kg | LS10lower | **-2.1** | **7.7** | . | . | 972.4 | **2.1** | **-16.0** |
| Conductivity | mS/m | F1 | . | **-11.1** | 63.2 | **7.3** | **-2.8** | . | **2.8** |
| | mS/m | F2 | . | **-17.0** | 52.3 | **-0.3** | **3.9** | . | **0.3** |
| | mS/m | F3 | . | **-12.0** | 72.7 | **-1.2** | **10.8** | . | **1.2** |
| | mS/m | F4 | . | 32.9 | **0.0** | **-22.4** | 46.7 | . | -25.7 |
| | mS/m | F5 | . | 57.8 | **0.0** | -48.7 | **5.1** | . | -29.0 |
| | mS/m | F6 | . | **0.5** | **-5.5** | -56.5 | **4.5** | . | **-0.6** |
| | mS/m | F7 | . | 38.5 | 28.3 | **-22.6** | -85.8 | 521.5 | 41.3 |
| Cr | mg/kg | F1 | -29.8 | 48.0 | 32.0 | . | -46.8 | 65.9 | -42.0 |
| | mg/kg | F2 | **5.3** | 98.8 | **2.4** | . | **-7.1** | . | -52.9 |
| | mg/kg | F3 | **9.6** | **-0.4** | **-13.5** | . | **11.9** | . | -48.5 |
| | mg/kg | F4 | **21.3** | 42.7 | -57.1 | . | 62.7 | . | -72.0 |
| | mg/kg | LS_2lower | **0.5** | 56.0 | . | . | 1106.0 | . | -43.5 |
| | mg/kg | LS10lower | **-21.9** | **21.3** | . | . | 838.0 | 155.6 | -55.6 |

Appendix 8 (2/3)

| Measurand | Unit | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| Cu | mg/kg | F1 | *31.8* | **3.6** | *141.6* | . | **0.0** | **-18.2** | *-44.5* |
| | mg/kg | F2 | **0.2** | **-6.0** | *34.0* | . | *56.8* | . | *-64.8* |
| | mg/kg | F3 | **0.9** | *-41.2* | *44.2* | . | *122.7* | . | *-50.9* |
| | mg/kg | F4 | **16.7** | . | **-15.5** | . | *114.3* | . | *-61.9* |
| | mg/kg | F5 | **13.4** | . | *75.6* | . | . | . | *-87.8* |
| | mg/kg | F6 | *53.1* | . | *44.1* | . | . | . | *-93.8* |
| | mg/kg | F7 | *30.3* | . | *60.0* | . | . | . | *-93.9* |
| | mg/kg | LS_2lower | *54.6* | **0.4** | . | . | *2515.4* | . | *-37.7* |
| | mg/kg | LS10lower | *115.2* | **13.5** | . | . | *2856.5* | **-13.5** | *-27.8* |
| DOC | mg/kg | F1 | . | . | *115.7* | . | *-63.7* | *-59.5* | *59.5* |
| | mg/kg | F2 | . | . | **21.2** | . | *-57.6* | . | *36.4* |
| | mg/kg | F3 | . | . | **8.3** | . | *-63.9* | . | *55.5* |
| | mg/kg | F4 | . | . | **6.5** | . | *-79.0* | . | *72.0* |
| | mg/kg | F5 | . | . | *27.7* | . | **21.6** | . | *-49.5* |
| | mg/kg | F6 | . | . | **4.9** | . | *56.9* | . | *-62.0* |
| | mg/kg | F7 | . | . | **-8.1** | . | *57.3* | . | *-49.2* |
| | mg/kg | LS10lower | . | . | . | . | *111.6* | *-85.5* | *-26.0* |
| F | mg/kg | F1 | . | . | *308.2* | . | *36.2* | *-86.7* | *-36.2* |
| | mg/kg | F2 | . | . | *65.6* | . | **6.1** | . | *-71.9* |
| | mg/kg | F3 | . | *-66.6* | *93.1* | . | *58.6* | . | *-58.6* |
| | mg/kg | F4 | . | **22.5** | **-22.5** | . | *73.4* | . | *-65.1* |
| | mg/kg | LS_2lower | . | **2.4** | . | . | *5863.9* | . | **-2.4** |
| | mg/kg | LS10lower | . | *-29.9* | . | . | *4088.3* | *43.2* | **-13.3** |
| Mo | mg/kg | F1 | **14.2** | *26.1* | **-13.6** | . | *-59.1* | *-42.4* | **16.4** |
| | mg/kg | F2 | *25.7* | **0.9** | **-3.3** | . | **18.3** | . | **-8.3** |
| | mg/kg | F3 | **-11.4** | **-3.2** | **-0.1** | . | *80.7* | . | **13.9** |
| | mg/kg | F4 | **-6.1** | *50.5* | *-29.7* | . | *39.4* | . | *-54.5* |
| | mg/kg | F5 | **9.7** | . | *58.1* | . | . | . | *-67.7* |
| | mg/kg | F6 | . | . | **3.2** | . | . | . | **-3.2** |
| | mg/kg | F7 | . | . | **0.0** | . | . | . | **0.0** |
| | mg/kg | LS_2lower | **0.0** | **5.9** | . | . | *1031.7* | . | **-5.0** |
| | mg/kg | LS10lower | **2.0** | **8.1** | . | . | *1054.5* | **-2.8** | **-2.3** |
| | mg/kg | LS10upper | **-16.4** | **0.0** | . | . | *844.3* | . | . |
| Pb | mg/kg | F1 | **-15.6** | **2.9** | *56.0* | . | *-37.5* | **14.6** | **-3.1** |
| | mg/kg | F2 | **-3.8** | **-15.9** | *32.9* | . | **-10.0** | . | **-1.3** |
| | mg/kg | F3 | **12.1** | **-14.3** | **-19.7** | . | **12.1** | . | **2.9** |
| | mg/kg | F4 | **-1.2** | **5.9** | **2.4** | . | **15.9** | . | **-24.4** |
| | mg/kg | F5 | *-51.6* | . | *31.6* | . | **15.8** | . | **-15.8** |
| | mg/kg | F6 | **-6.3** | . | **-20.6** | . | **6.3** | . | **25.0** |
| | mg/kg | F7 | **0.0** | . | *-34.2* | . | . | . | *33.3* |
| | mg/kg | LS_2lower | **2.6** | **-4.4** | . | . | *930.8* | . | **-1.0** |
| | mg/kg | LS10lower | **2.1** | **-13.3** | . | . | *846.5* | **-0.7** | **1.9** |

| Measurand | Unit | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| pH | | F1 | **0.7** | **2.9** | **-7.4** | **0.7** | **6.3** | **-2.2** | **-0.5** |
| | | F2 | **-0.7** | **2.2** | **-6.6** | **-0.7** | **6.0** | . | **-0.7** |
| | | F3 | **0.0** | **1.4** | **-8.0** | **-0.7** | **5.9** | . | **-1.7** |
| | | F4 | **0.8** | **-2.3** | **-4.5** | **0.8** | **6.3** | . | **-1.0** |
| | | F5 | **0.0** | **1.6** | **-1.6** | **0.0** | **2.3** | . | **-0.4** |
| | | F6 | **0.0** | **2.4** | **-3.1** | **-2.4** | **1.1** | . | **-0.6** |
| | | F7 | **0.8** | **2.4** | **-3.1** | **-2.4** | **1.0** | **1.6** | **-0.3** |
| Sb | mg/kg | F1 | *-45.7* | . | *85.7* | . | . | . | *-42.9* |
| | mg/kg | F2 | *-26.3* | . | **21.1** | . | . | . | **5.3** |
| | mg/kg | F3 | *-74.7* | . | *141.4* | . | . | . | *-65.5* |
| | mg/kg | F4 | *-67.7* | . | *135.5* | . | . | . | *-67.7* |
| Se | mg/kg | F1 | **18.4** | *53.1* | **2.7** | . | *-68.6* | . | **-6.1** |
| | mg/kg | F2 | **24.0** | . | **-19.6** | . | **18.0** | . | **-24.0** |
| | mg/kg | F3 | **-21.9** | *65.3* | *-55.9* | . | *45.3* | . | *-37.5* |
| | mg/kg | F4 | *46.8* | . | *-48.9* | . | *217.0* | . | *-57.4* |
| | mg/kg | LS_2lower | **10.0** | **16.4** | . | . | *1008.2* | . | **-20.9** |
| | mg/kg | LS10lower | **10.0** | **16.4** | . | . | *1008.2* | . | **-19.1** |
| SO4 | mg/kg | F1 | *-28.9* | **-6.4** | *31.9* | . | *-35.3* | **6.4** | *27.7* |
| | mg/kg | F2 | *-27.4* | **0.0** | *30.4* | . | **-2.3** | . | *30.4* |
| | mg/kg | F3 | **14.0** | **1.5** | **0.0** | . | **-13.3** | . | **-24.9** |
| | mg/kg | F4 | *40.8* | **15.2** | *-78.7* | . | **0.0** | . | *-73.3* |
| | mg/kg | F5 | *164.4* | *5431.6* | *43.7* | . | *-43.7* | . | *-51.1* |
| | mg/kg | F6 | *362.5* | **-3.4** | . | . | *-75.9* | . | **3.4** |
| | mg/kg | F7 | . | **16.3** | . | . | *-32.6* | . | **16.3** |
| | mg/kg | LS_2lower | **7.2** | **7.6** | . | . | *788.0* | . | **-14.8** |
| | mg/kg | LS10lower | **6.7** | **7.0** | . | . | *782.5* | **-6.7** | **-15.2** |
| V | mg/kg | F1 | *33.1* | **20.8** | **-14.5** | . | *-60.8* | . | **-3.1** |
| | mg/kg | F2 | *30.0* | **1.0** | *-47.8* | . | *37.0* | . | **-22.0** |
| | mg/kg | F3 | *36.4* | **-6.4** | *-37.1* | . | *219.1* | . | **2.7** |
| | mg/kg | F4 | *45.0* | . | *-49.5* | . | *350.0* | . | *-45.0* |
| | mg/kg | LS_2lower | *33.6* | **0.3** | . | . | *1577.8* | . | **-8.9** |
| | mg/kg | LS10lower | *33.6* | **0.3** | . | . | *1577.8* | . | **-8.9** |
| Zn | mg/kg | F1 | . | **20.2** | *69.1* | . | *-46.2* | **0.0** | **-19.6** |
| | mg/kg | F2 | . | **2.8** | *30.3* | . | **-2.8** | . | *-38.2* |
| | mg/kg | F3 | . | *-30.1* | *29.2* | . | *52.1* | . | *-37.6* |
| | mg/kg | F4 | . | *46.4* | *-46.4* | . | *92.4* | . | *-65.5* |
| | mg/kg | F5 | . | *183.3* | **-13.8** | . | **13.6** | . | *-76.3* |
| | mg/kg | F6 | . | *42.3* | *-47.3* | . | *88.3* | . | *-41.5* |
| | mg/kg | F7 | . | *37.8* | *-38.4* | . | *33.8* | . | *-33.0* |
| | mg/kg | LS_2lower | . | **22.3** | . | . | *1338.9* | . | **-22.3** |
| | mg/kg | LS10lower | . | **15.1** | . | . | *1247.5* | **12.2** | *-27.0* |

The D% values ≤ | 25 % | written in bold and D% values > | 25 % | written in italics.

The share of D% values ≤ | 25 % |, % in all: 51 %

## Appendix 9. Summary of the z scores

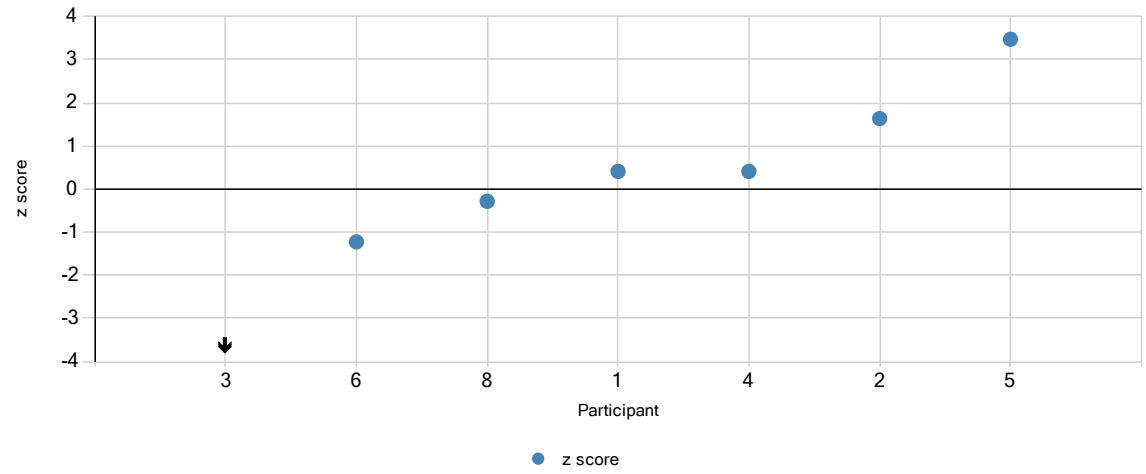
| Measurand | Sample | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | | % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | F1 | *S* | **S** | u | **S** | *U* | **S** | . | **S** | . . . . . | 71.4 |
| | F2 | *S* | **S** | u | **S** | *U* | . | . | **S** | . . . . . | 66.7 |
| | F3 | *S* | **S** | u | **S** | *U* | . | . | **S** | . . . . . | 66.7 |
| | F4 | *S* | **S** | q | **S** | *U* | . | . | **S** | . . . . . | 66.7 |
| | F5 | *S* | **S** | S | **S** | *S* | . | . | **S** | . . . . . | 100 |
| | F6 | *S* | **S** | S | **S** | *S* | . | . | **S** | . . . . . | 100 |
| | F7 | *S* | **S** | S | **S** | *S* | **S** | . | **S** | . . . . . | 100 |
| % | | 100 | 100 | 43 | 100 | 43 | 100 | | 100 | | |
| accredited | | | 7 | | 7 | | 2 | | 7 | | |

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

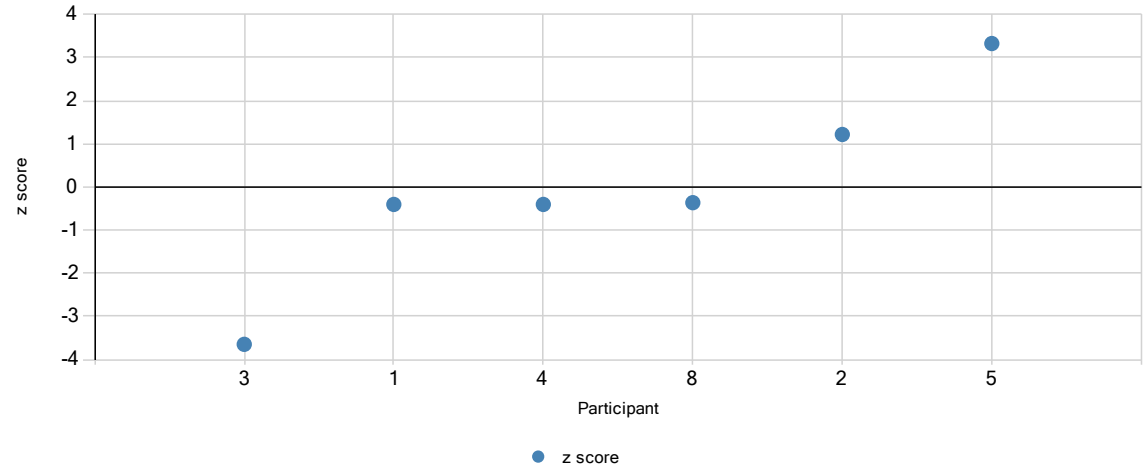
Totally satisfactory, % in all: 82 % in accredited: 100 % in non-accredited: 71

## Appendix 10.z scores in ascending order

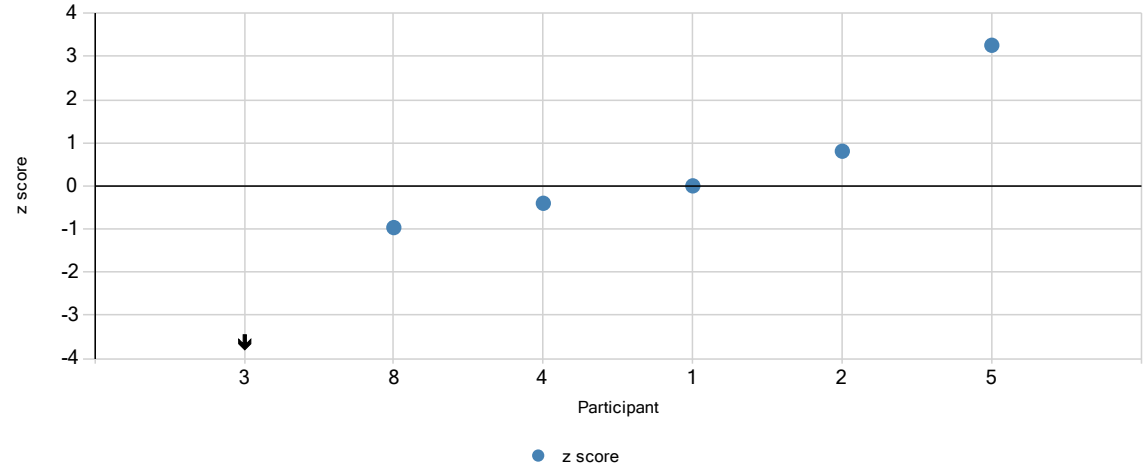
Measurand pH Sample F1

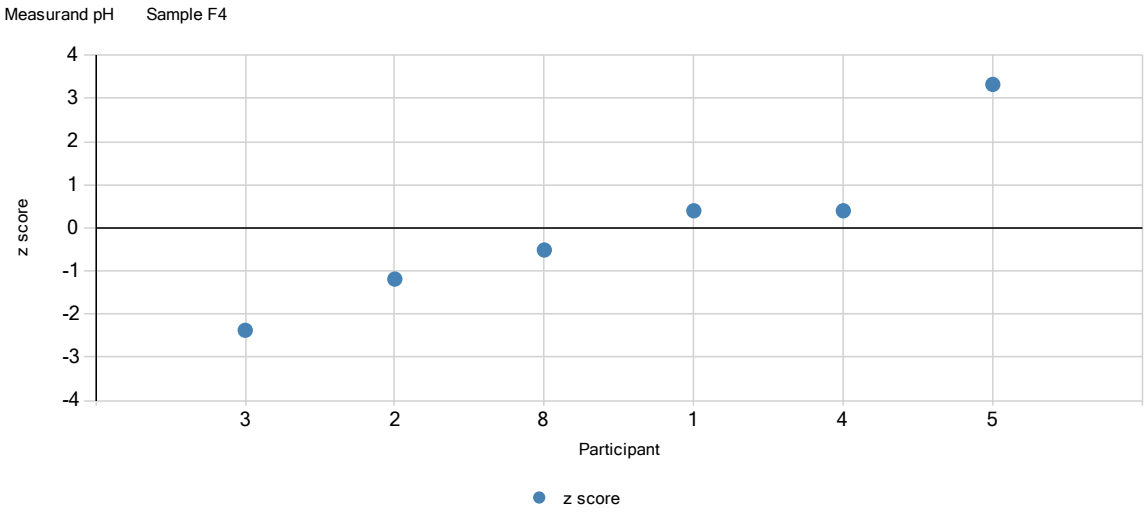


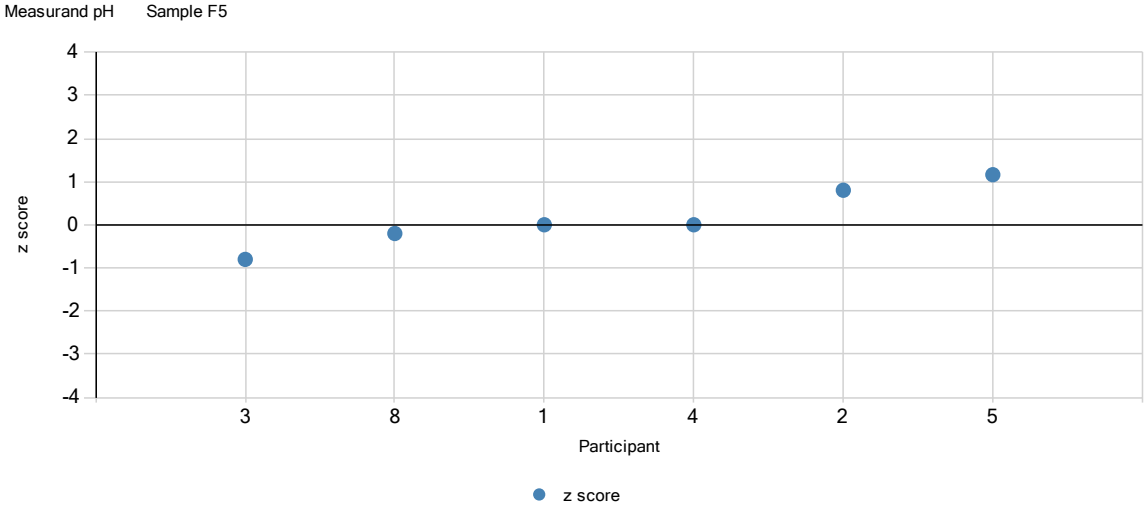

Measurand pH Sample F2

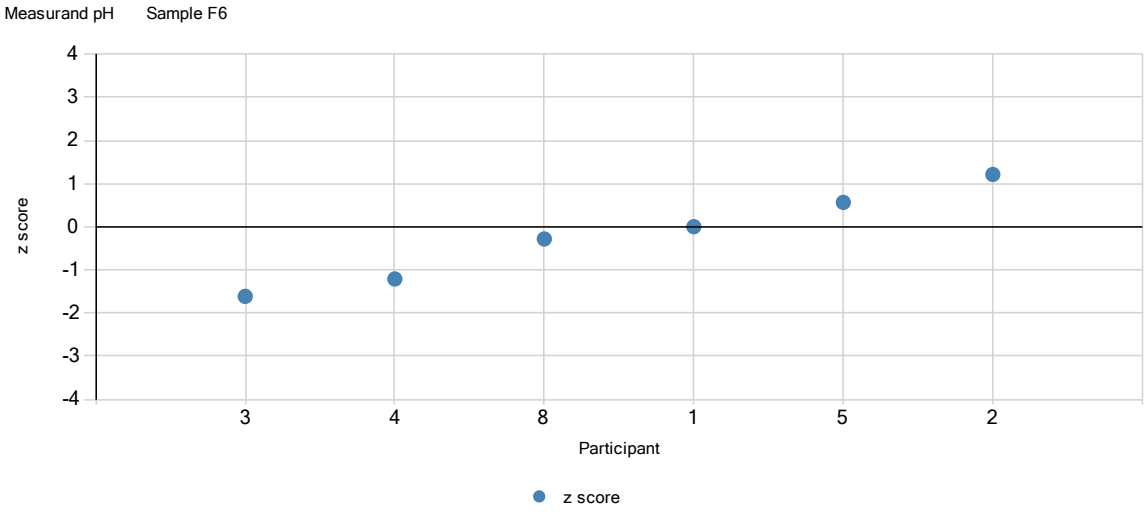


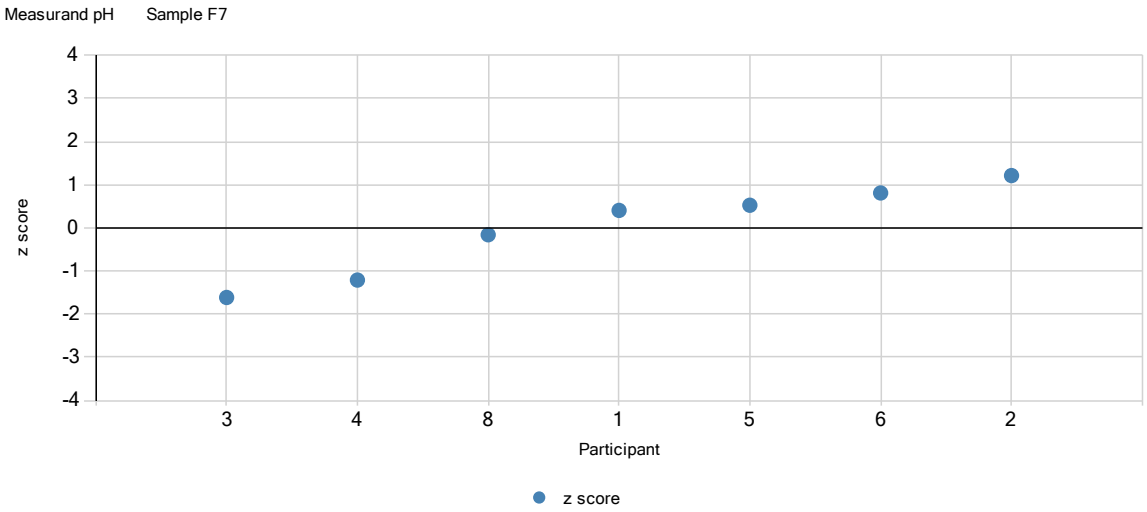

Measurand pH Sample F3




Measurand pH Sample F4
z score
4
3
2
1
0
-1
-2
-3
-4
3
2
8
1
4
5
Participant
z score


Measurand pH Sample F5
z score
4
3
2
1
0
-1
-2
-3
-4
3
8
1
4
2
5
Participant
z score


Measurand pH Sample F6
z score
4
3
2
1
0
-1
-2
-3
-4
3
4
8
1
5
2
Participant
z score


Measurand pH
Sample F7
z score
4
3
2
1
0
-1
-2
-3
-4
3
4
8
1
5
6
2
Participant
z score

## Appendix 11. Up-flow percolation test, production of eluates

| Start date of the up-flow percolation test | Sample amount, Mw (kg) | Description of the column: length, diameter | Duration of the fraction | | | | | | | End date of the up-flow percolation test | How do you treat, in general, the results which are below the limit of detection when reporting the cumulative results (e.g. L/S 2 or L/S 10) to the customers? |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Fraction 1, L/S 0.1 | Fraction 2, L/S 0.1 | Fraction 3, L/S 0.3 | Fraction 4, L/S 0.5 | Fraction 5, L/S 1.0 | Fraction 6, L/S 3.0 | Fraction 7, L/S 5.0 | | |
| 1.4.2021 | 528.1 | Length 30 cm Diameter 5 cm | 1.4 h | 5.4 | - | 12.5 | 20.8 | - | 125 | 23.4.2021 | - |
| 2.4.2021 | 1.78 | Length 28 cm Diameter 10 cm | 3 d | - | - | - | - | - | - | 19 days | We only use LOQ values and add them together to and sum and make it a "less than" values. |
| 12.4.2021 | 0.398951 | Length 40.2 cm Diameter 4.8 cm | 3 h 30 min | 2 h 50 min | 6 h 20 min | 26 h 40 min | 38 h 45 min | 72 h 45 min | 192 h 45 min | 27.4.2021 | When the result for one or more fractions is below the limit of quantification, L/S 2 and L/S 10 are given as below LOQ results and increasing the LOQ to the value of the calculated L/S 2 or L/S 10. For example, if LOQ is 0.05 and L/S 10 value is 0.06 (and in calculations one fraction is below the LOQ), the reported result is < 0.06. |
| 19.4.2021 | 0.558 | Length 35 cm Diameter 5 cm | 5 h | 5 h | 15 h | 1 d 1 h | 1 d 23 h | 6 d 3 h | 11 d | 10.5.2021 | - |
| 22.4.2021 | 0.5005 | Length 55 cm Diameter 5 cm | 4 h | 4 h | 16 h | 22 h | 45 h | 144 h | 216 h | 17.5.2021 | The < LOQ result is directly used for calculations. |
| 3.5.2021 | 0.5897 | Length 30 cm Diameter 5 cm | 4.79 h | 4.79 h | 14.38 h | 23.97 h | 47.94 h | 143.83 h | 239.72 h | 24.5.2021 | The results are reported as below the limit of detection. |

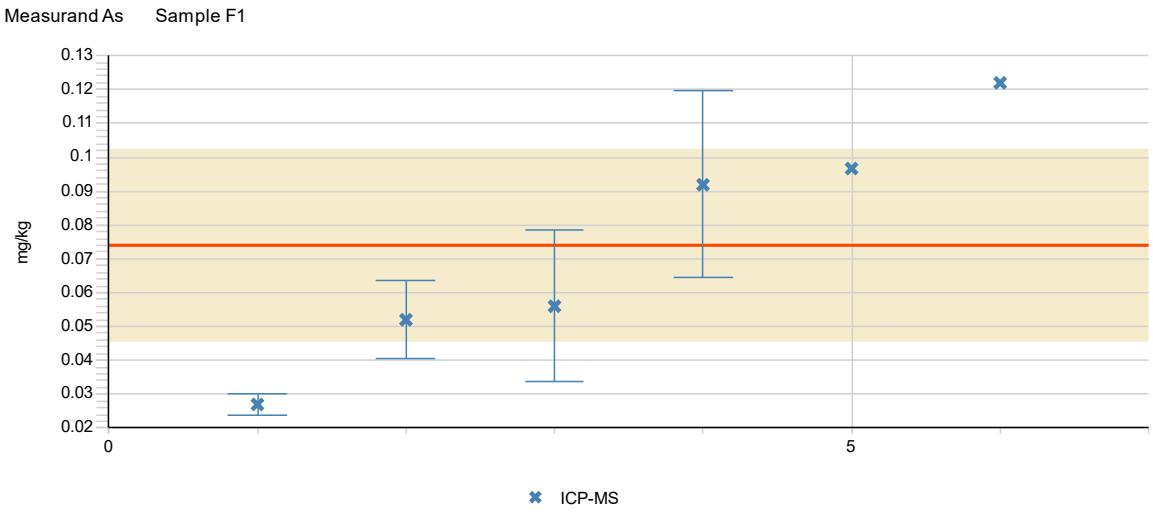
## Appendix 12. Method of analysis by measurands

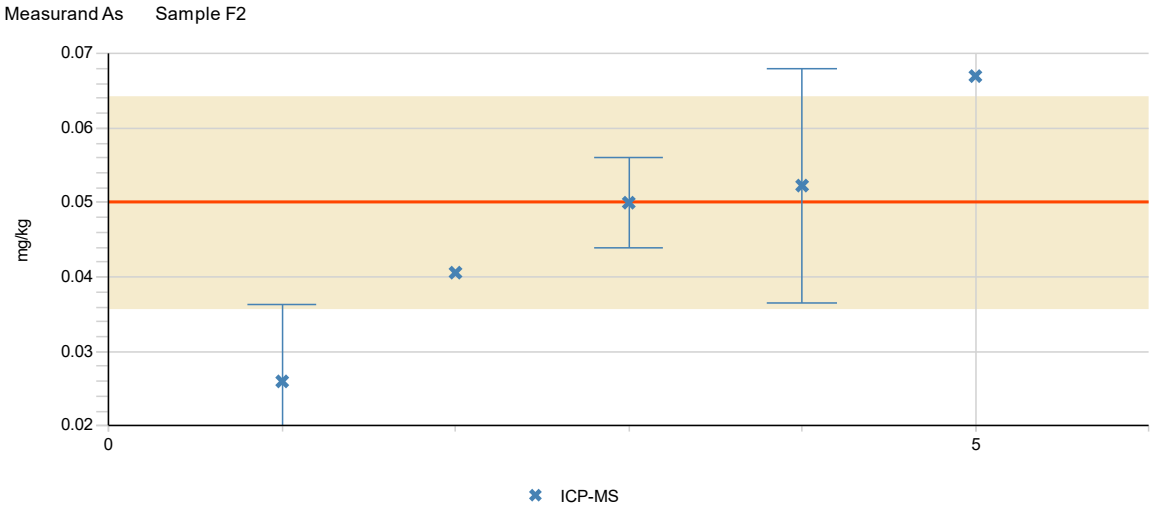
| Measurand | Standard options | No. of partici-pants | Applied / modified / more information | No. of partici-pants |
|---|---|---|---|---|
| As n=5 (the number of participants who answered) | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| Ba n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| Cd n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| $Cl^-$ n=5 | ISO 9297:1989 | 1 | Applied standard | 1 |
| | EN ISO 10304-1:2009 | 4 | Applied standard | 3 |
| | | | Internal method, based on this standard | 1 |
| Conductivity n=5 | EN 27888:1993 | 4 | Applied standard | 2 |
| | | | Internal method, based on this standard | 2 |
| | Other method | 1 | Applied standard: ISO 7888:1995 | 1 |
| Cr n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| Cu n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| DOC n=5 | EN 1484:1997 | 4 | Applied standard | 3 |
| | | | Internal method, based on this standard | 1 |
| | Other method | 1 | Applied standard: APHA 5310 B | 1 |
| $F^-$ n=5 | EN ISO 10304-1:2009 | 4 | Applied standard | 3 |
| | | | Internal method, based on this standard | 1 |
| | Other method | 1 | Applied standard: APHA 4500-F- D | 1 |
| Hg n=5 | EN ISO 17852:2008 | 1 | Applied standard | 1 |
| | Other method | 6 | Internal method, based on standard: EN ISO 17294-1:2006 | 2 |
| | | | Internal method, based on standard: EN ISO 17294-2:2006 | 1 |
| | | | Internal method, based on standard: EN 1483:2007 | 1 |
| | | | Internal method, based on standard: EN ISO 15587-2:2002 | 1 |
| | | | Modified: EN ISO 17294-2:2016 | 1 |

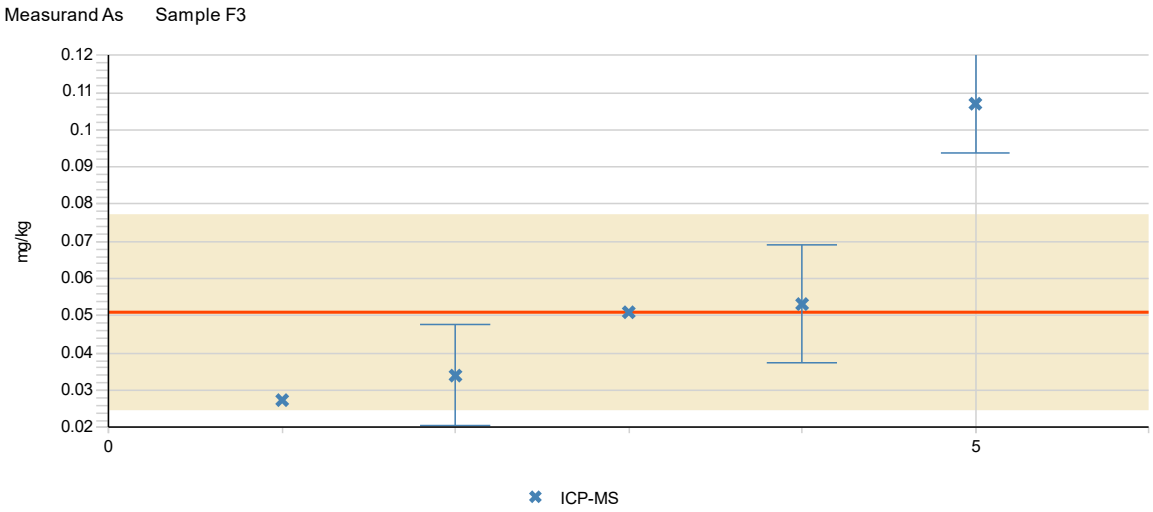
| Measurand | Standard options | No. of partici-pants | Applied / modified / more information | No. of partici-pants |
|---|---|---|---|---|
| Mo n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| Ni n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| Pb n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| pH n=5 | ISO 10523:2012 | 5 | Applied standard | 4 |
| | | | Internal method, based on this standard | 1 |
| Sb n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| Se n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |
| $SO_4^{2-}$ n= | EN ISO 10304-1:2009 | 4 | Applied standard | 3 |
| | | | Internal method, based on this standard | 1 |
| | Other method | 1 | Internal method, based on this standard: APHA 4500-SO42- E | 1 |
| V n=4 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 4 | Applied standard | 2 |
| | | | Internal method, based on this standard | 2 |
| Zn n=5 | EN ISO 17294-1:2006 | 3 | Applied standard | 1 |
| | | | Internal method, based on this standard | 2 |
| | EN ISO 17294-2:2016 | 5 | Applied standard | 3 |
| | | | Internal method, based on this standard | 2 |

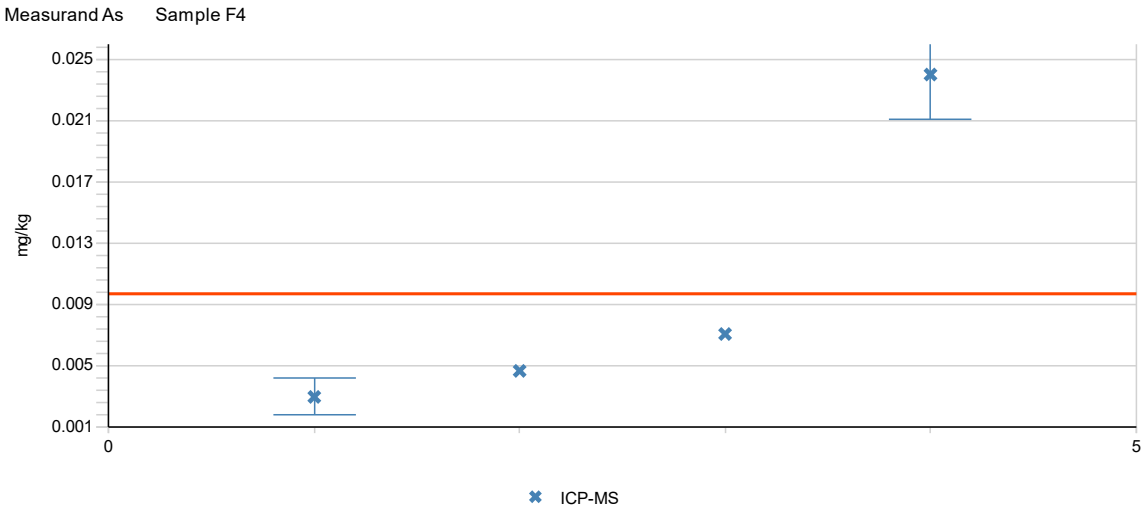
## Appendix 13. Results grouped according to the methods

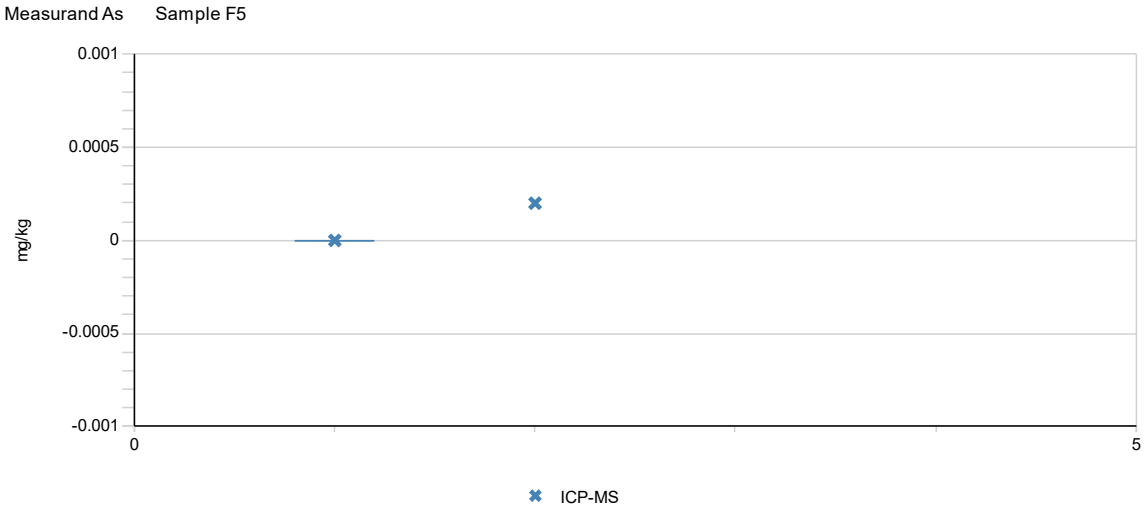
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



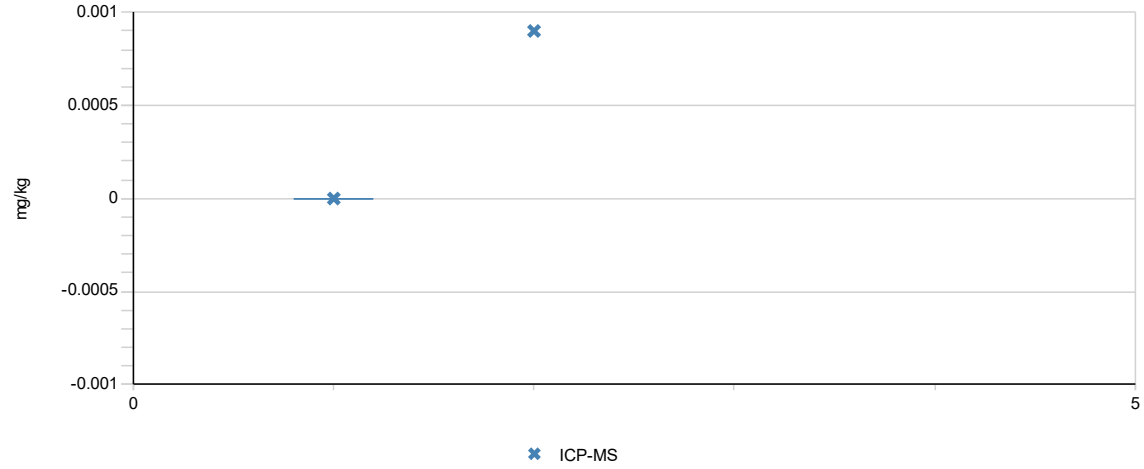




Measurand As
Sample F3
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
mg/kg
0
5
ICP-MS

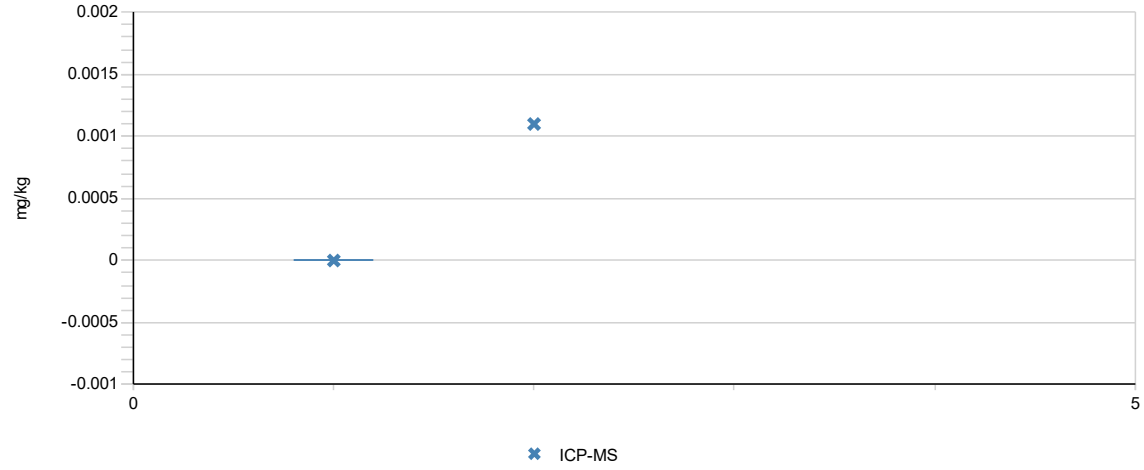

Measurand As
Sample F4
0.025
0.021
0.017
0.013
0.009
0.005
0.001
mg/kg
0
5
ICP-MS


Measurand As
Sample F5
0.001
0.0005
0
-0.0005
-0.001
mg/kg
0
5
ICP-MS

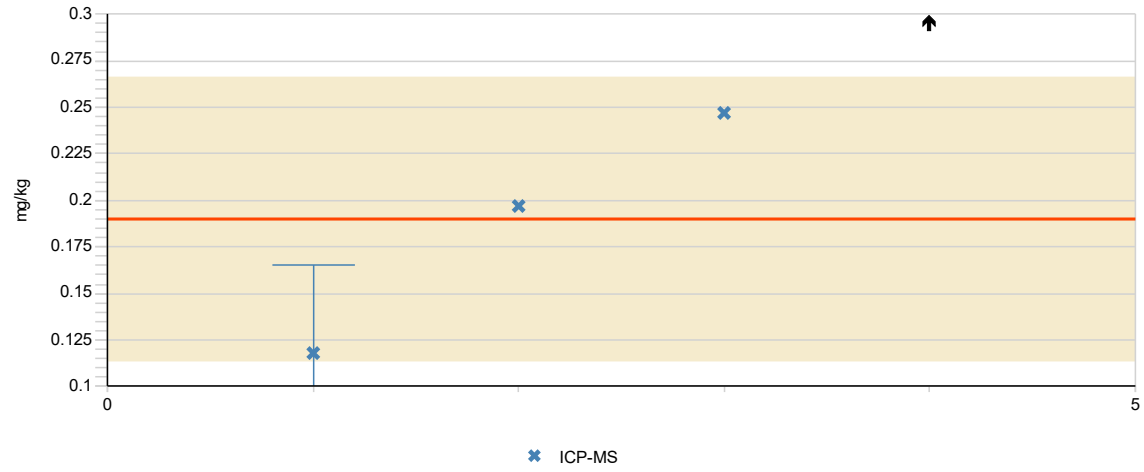
Measurand As Sample F6

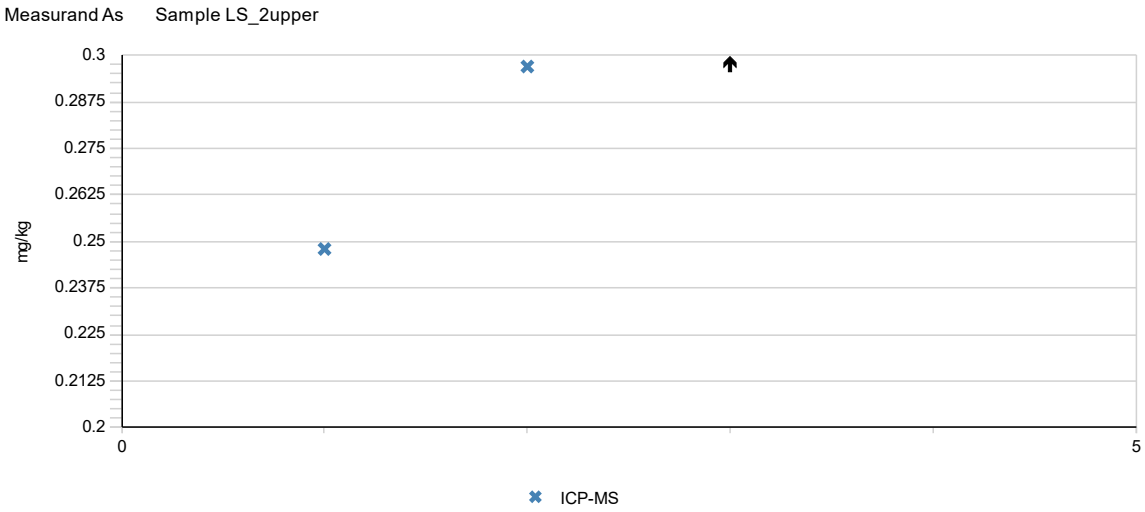


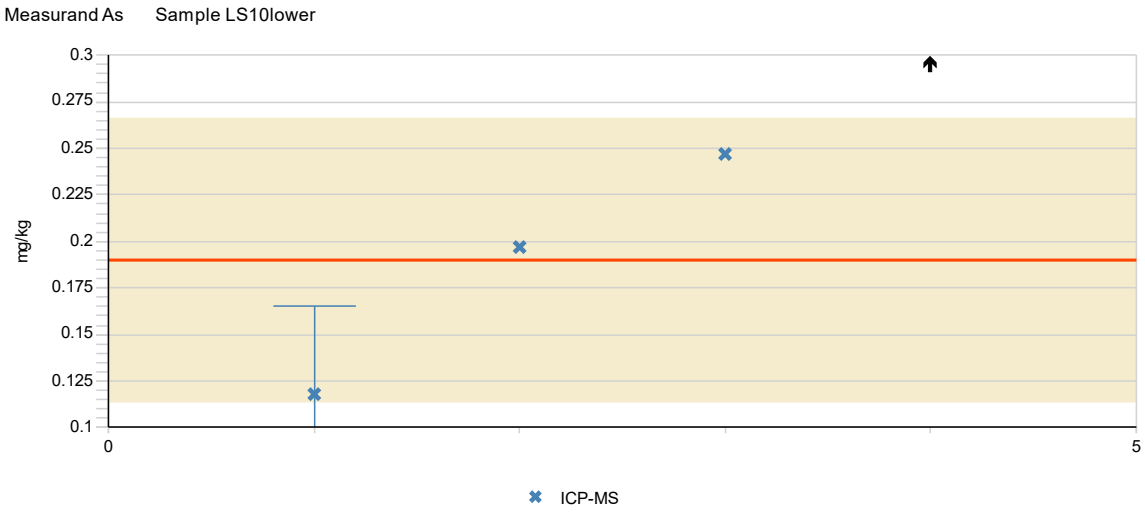

Measurand As Sample F7

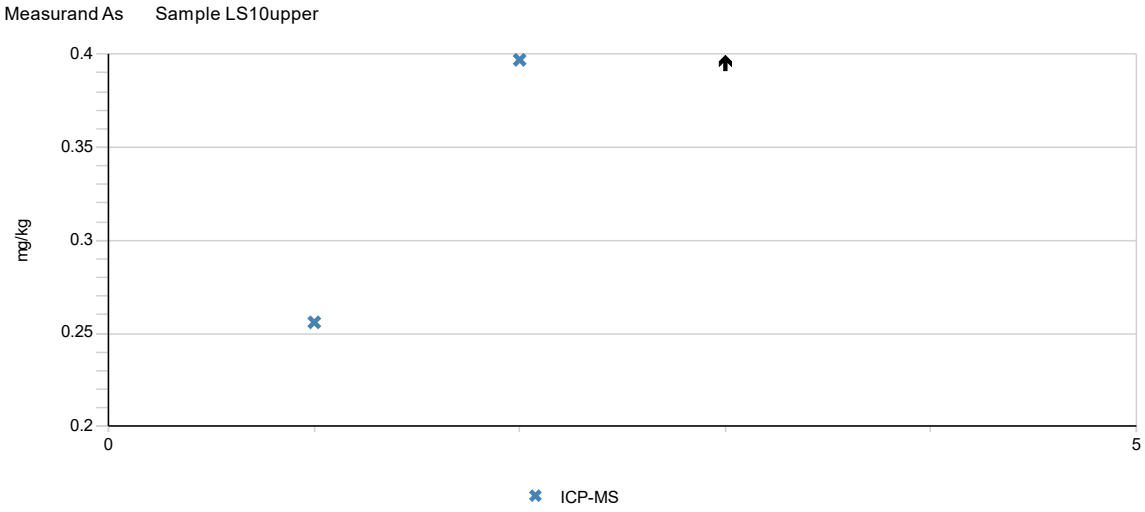



Measurand As Sample LS_2lower

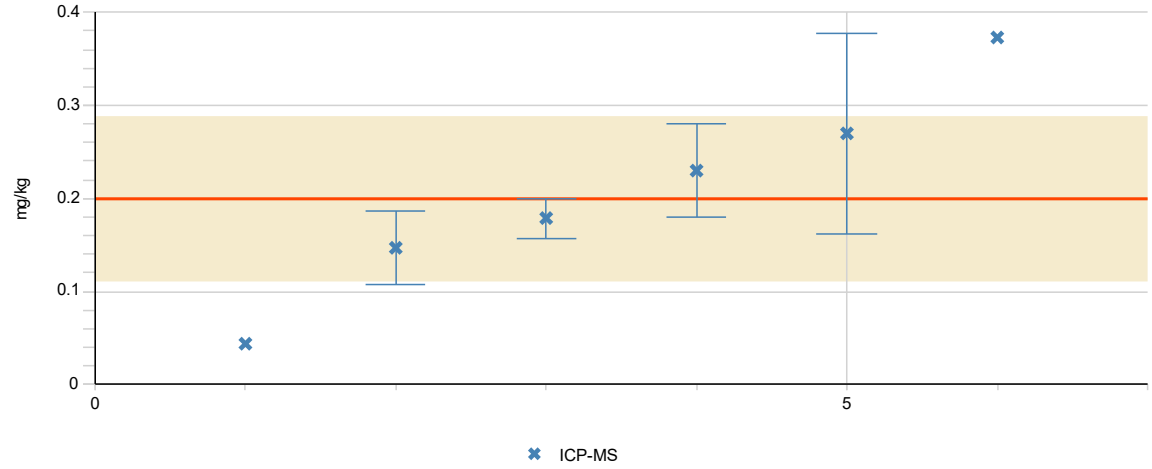



Measurand As
Sample LS_2upper
0.3
0.2875
0.275
0.2625
0.25
0.2375
0.225
0.2125
0.2
mg/kg
0
5
ICP-MS

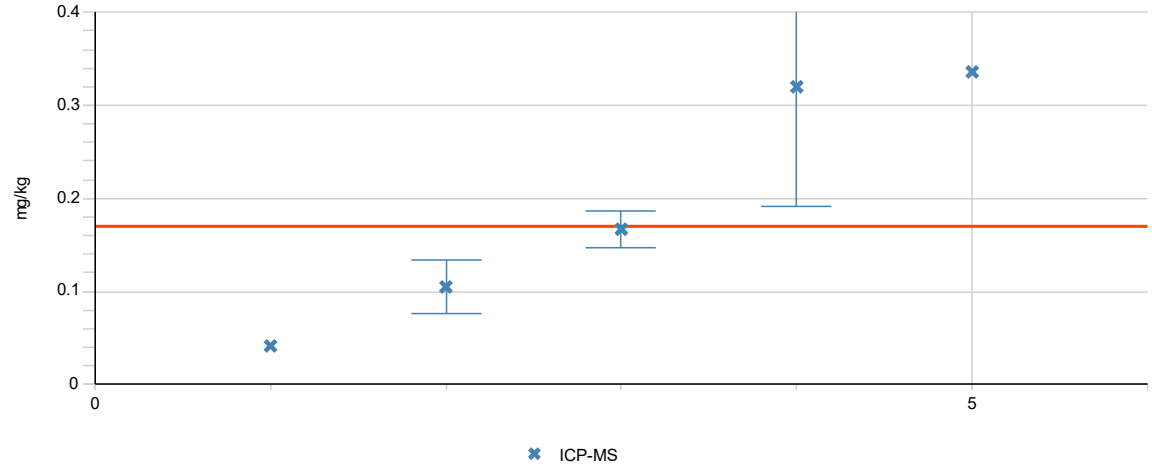

Measurand As
Sample LS10lower
0.3
0.275
0.25
0.225
0.2
0.175
0.15
0.125
0.1
mg/kg
0
5
ICP-MS


Measurand As
Sample LS10upper
0.4
0.35
0.3
0.25
0.2
mg/kg
0
5
ICP-MS

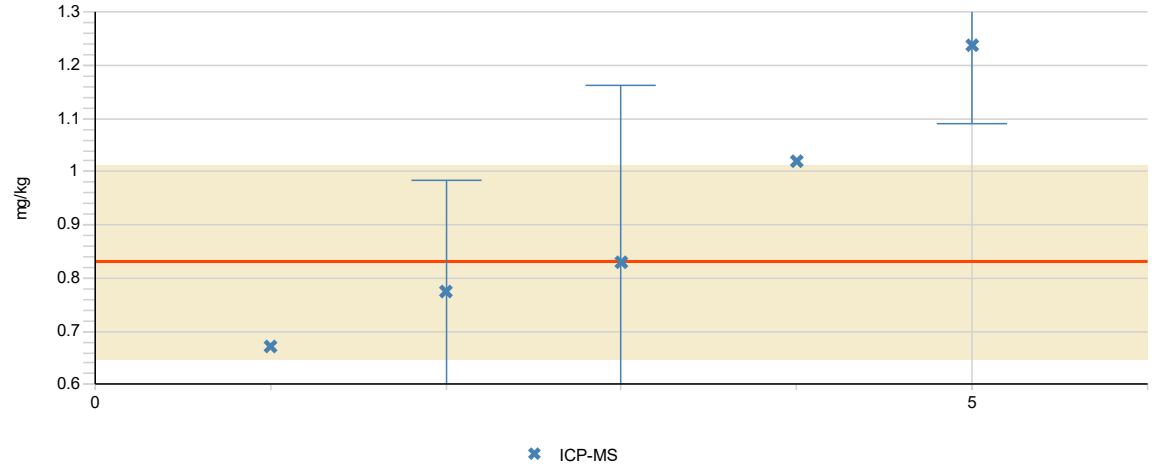
Measurand Ba Sample F1

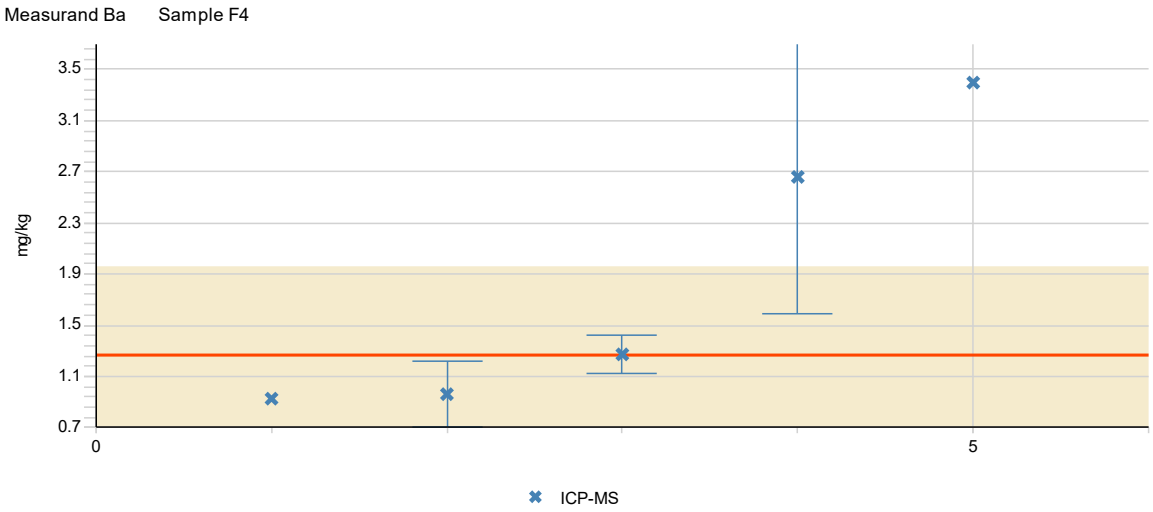


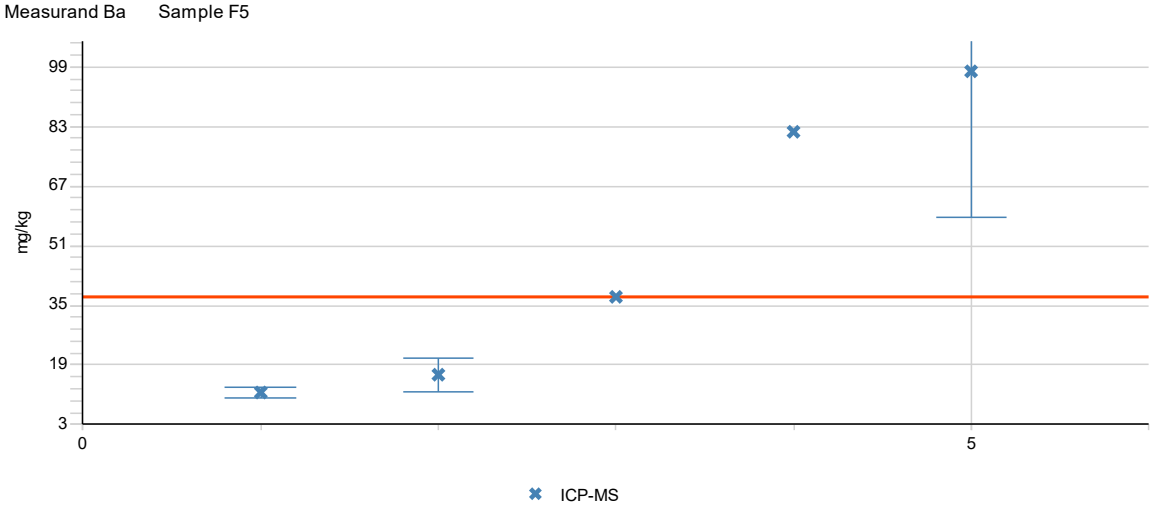

Measurand Ba Sample F2

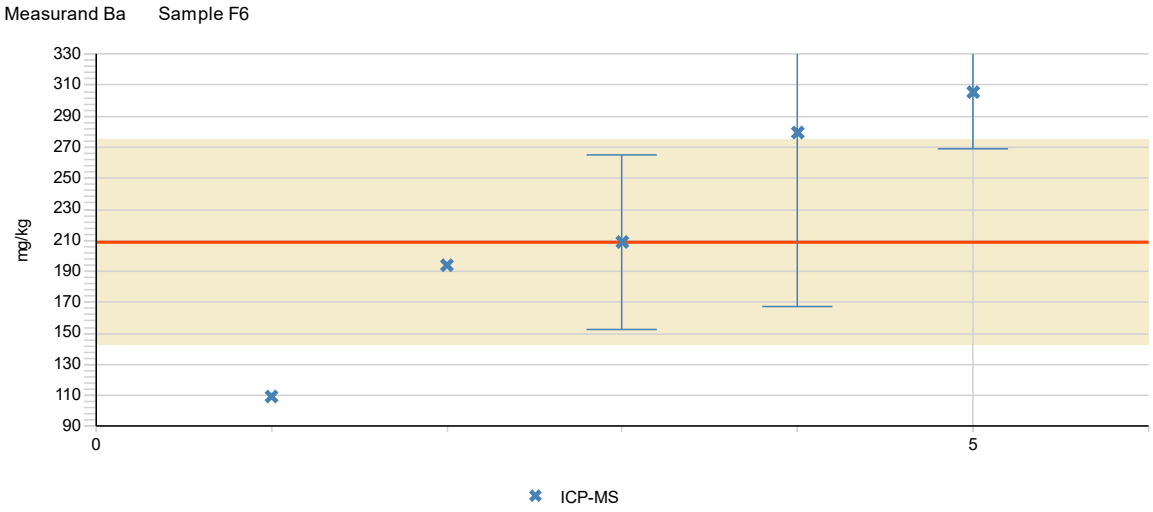



Measurand Ba Sample F3

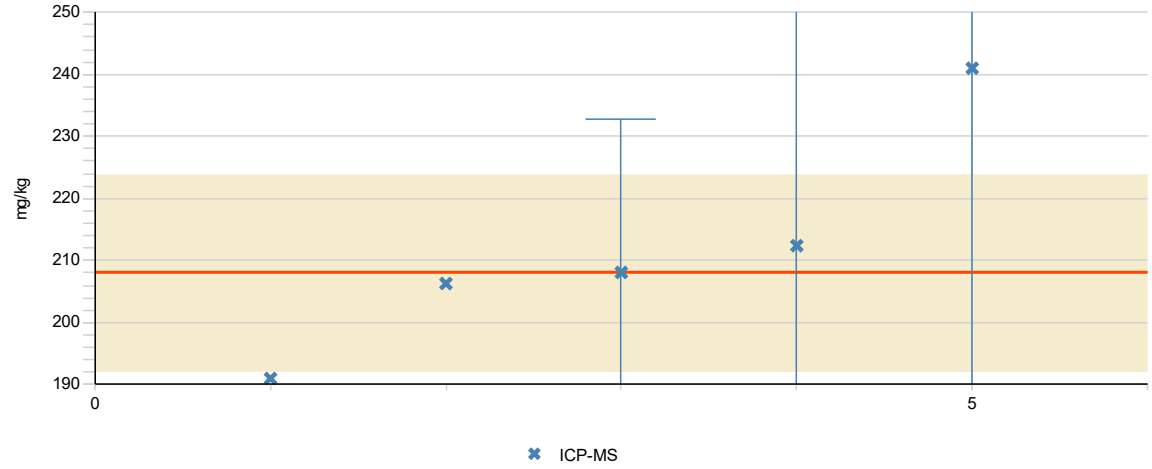



Measurand Ba
Sample F4
mg/kg
3.5
3.1
2.7
2.3
1.9
1.5
1.1
0.7
0
5
ICP-MS

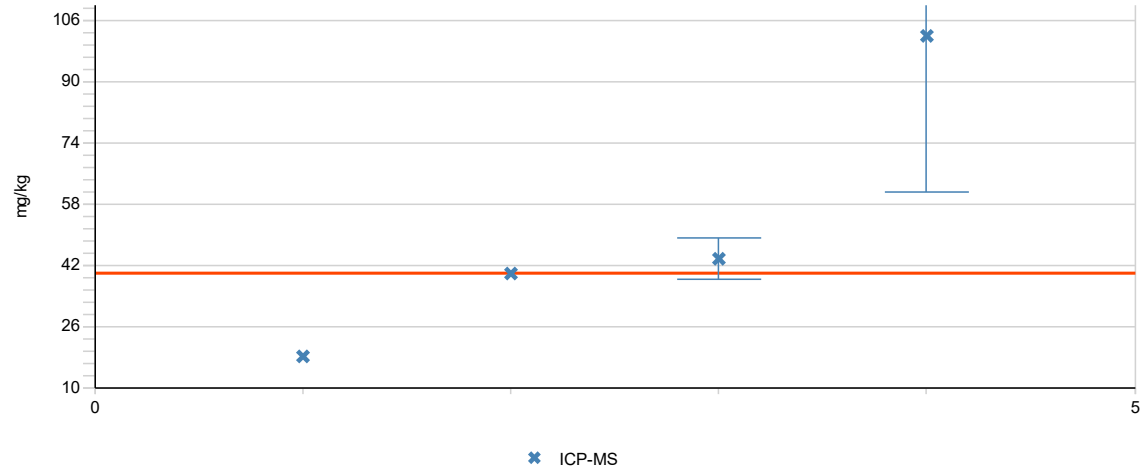

Measurand Ba
Sample F5
mg/kg
99
83
67
51
35
19
3
0
5
ICP-MS


Measurand Ba
Sample F6
mg/kg
330
310
290
270
250
230
210
190
170
150
130
110
90
0
5
ICP-MS

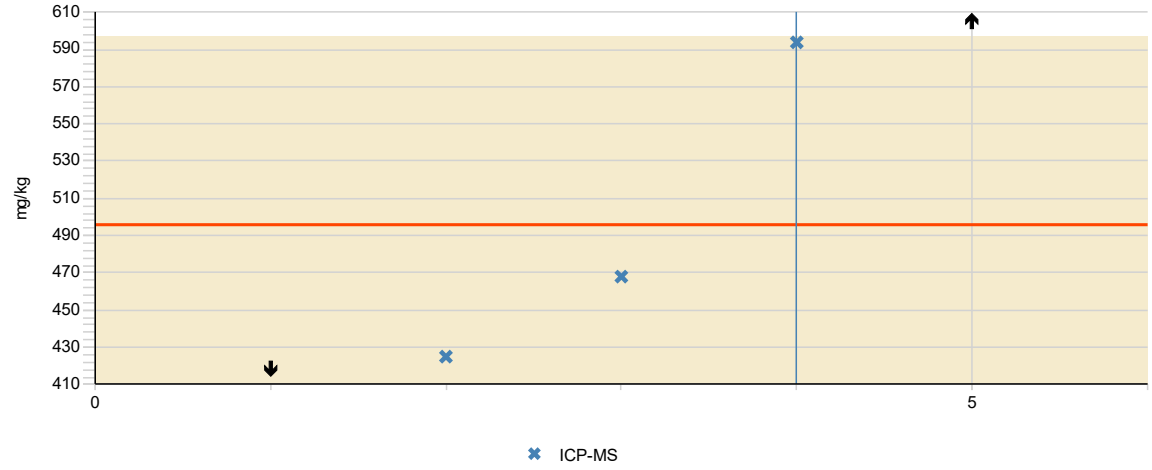
Measurand Ba Sample F7

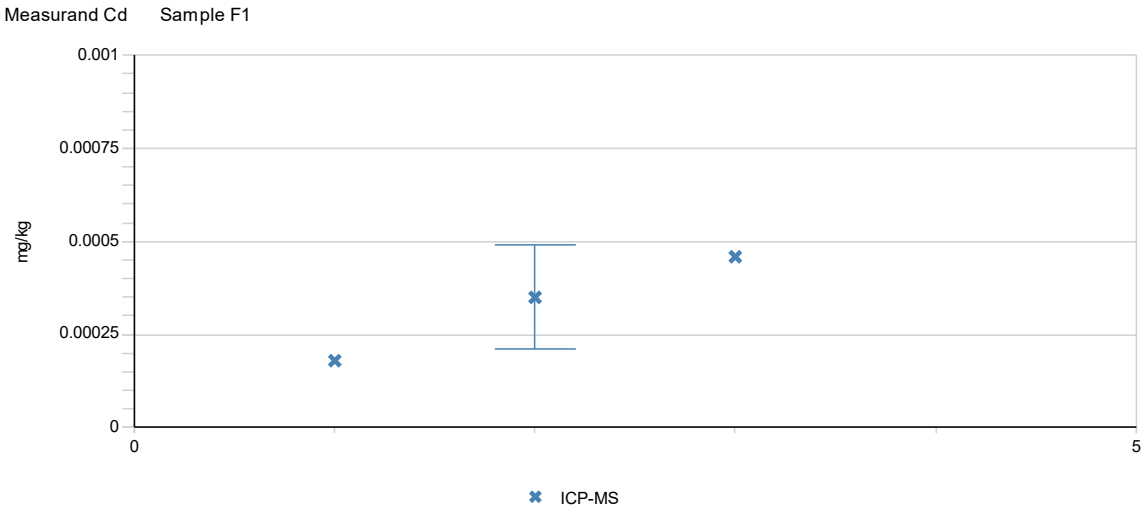


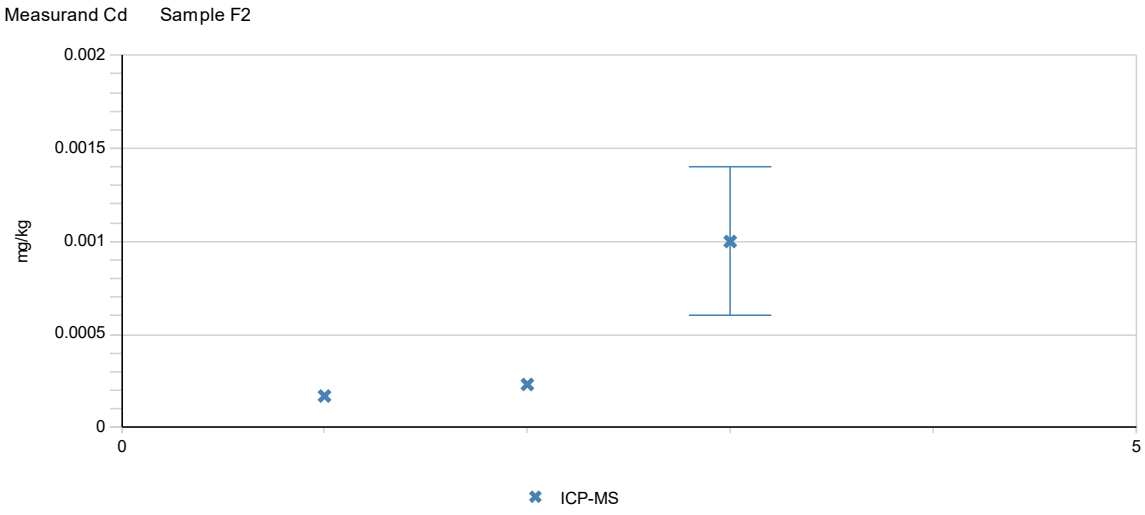

Measurand Ba Sample LS_2lower

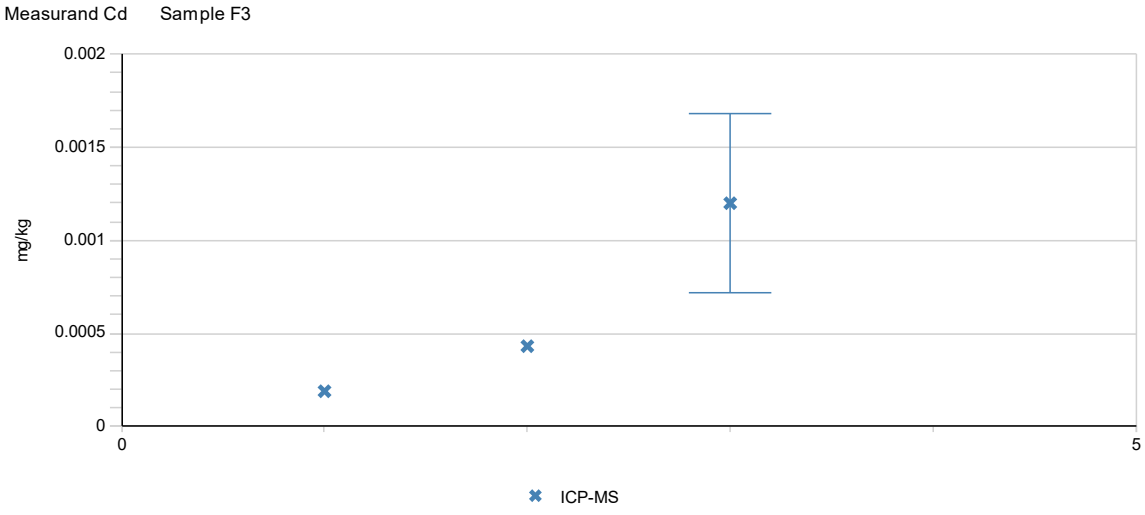


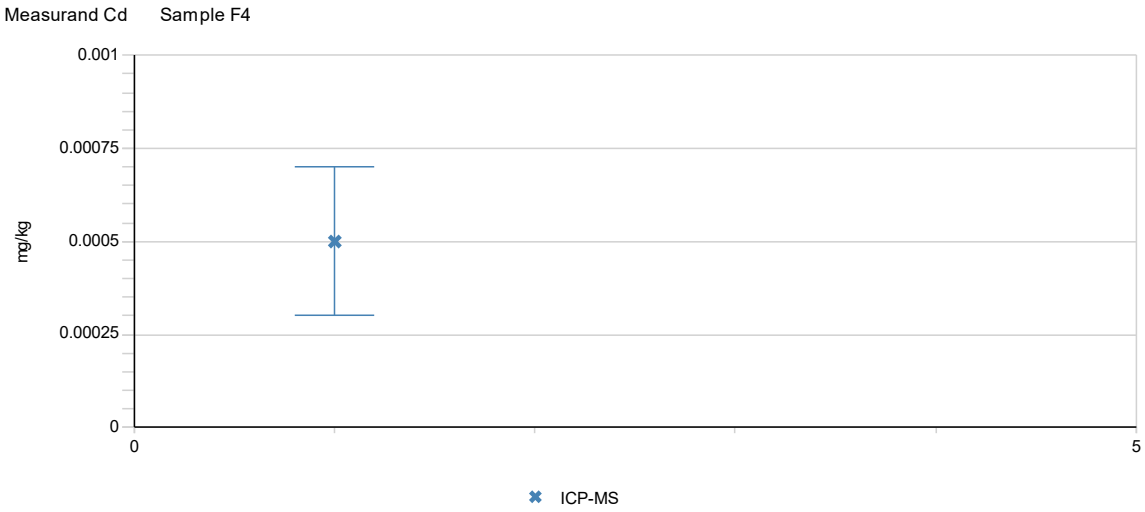

Measurand Ba Sample LS10lower

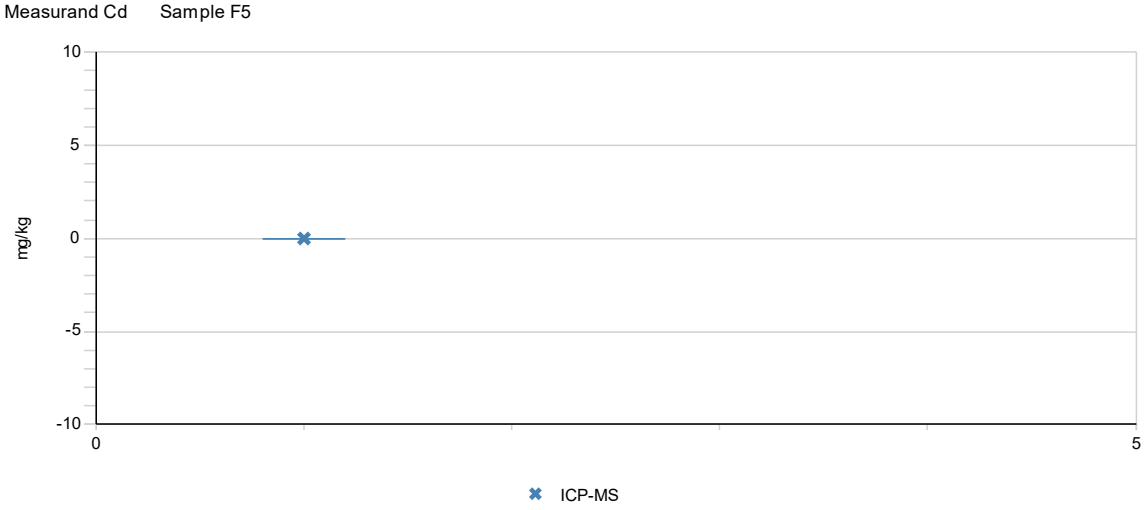


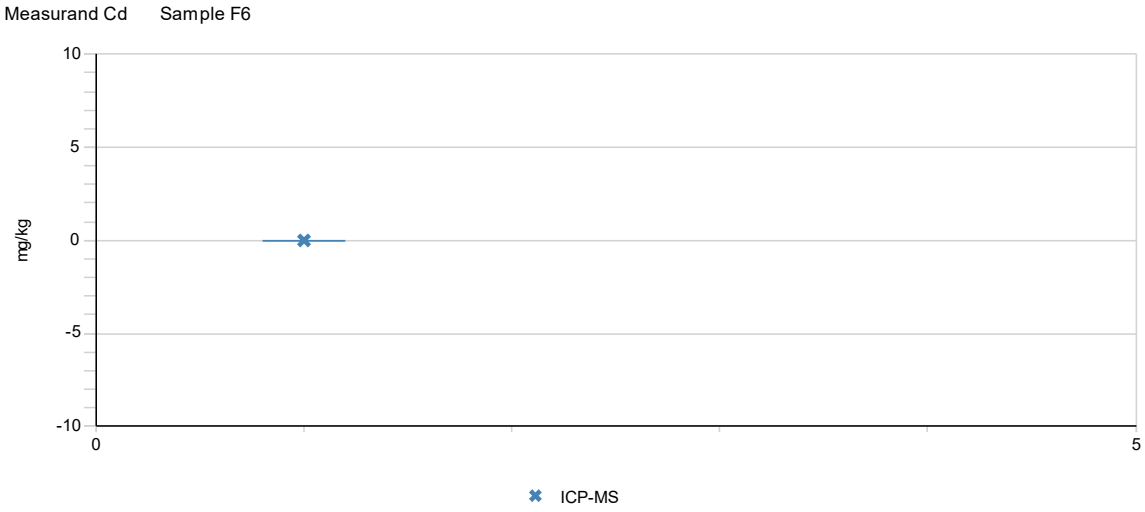

Measurand Cd Sample F1
0.001
0.00075
0.0005
0.00025
0
mg/kg
0
5
ICP-MS

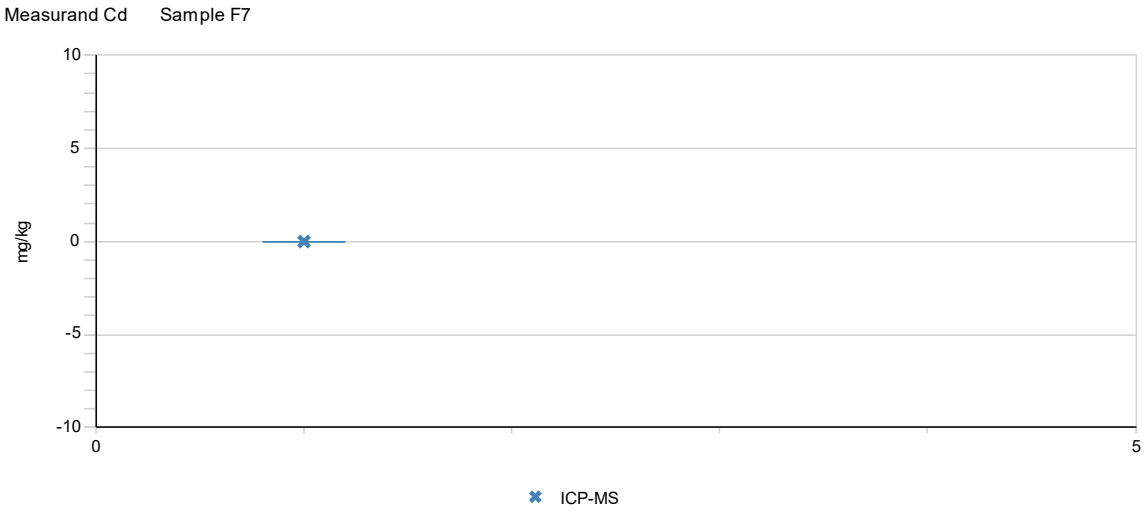

Measurand Cd Sample F2
0.002
0.0015
0.001
0.0005
0
mg/kg
0
5
ICP-MS

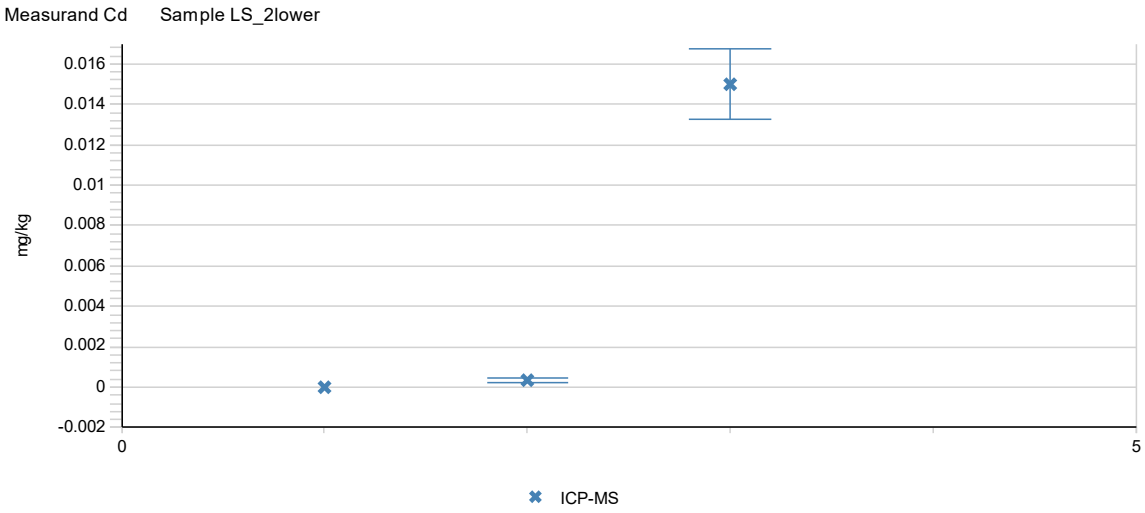

Measurand Cd Sample F3
0.002
0.0015
0.001
0.0005
0
mg/kg
0
5
ICP-MS

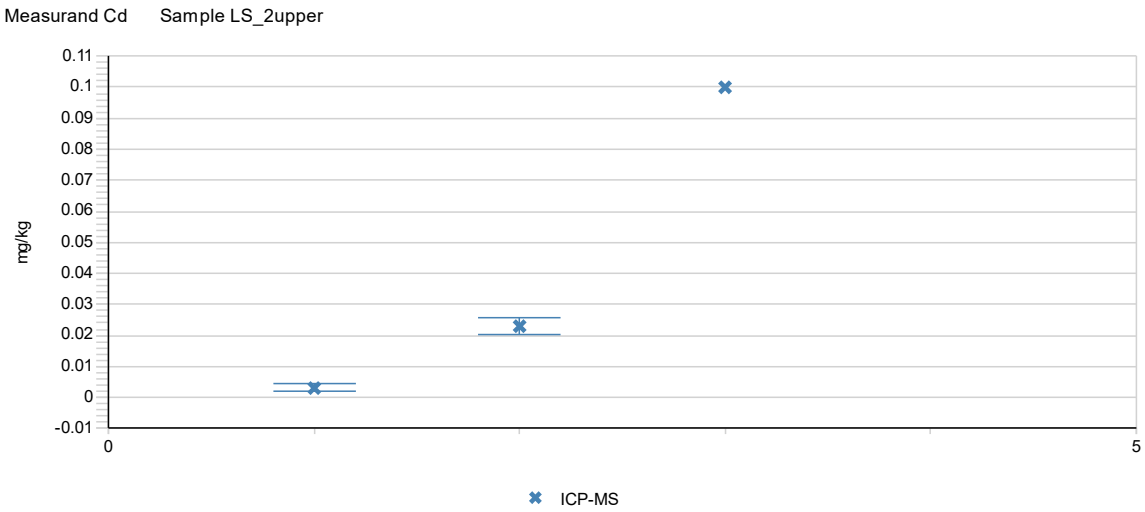

Measurand Cd Sample F4
0.001
0.00075
0.0005
0.00025
0
mg/kg
0
5
ICP-MS


Measurand Cd Sample F5
10
5
0
-5
-10
mg/kg
0
5
ICP-MS

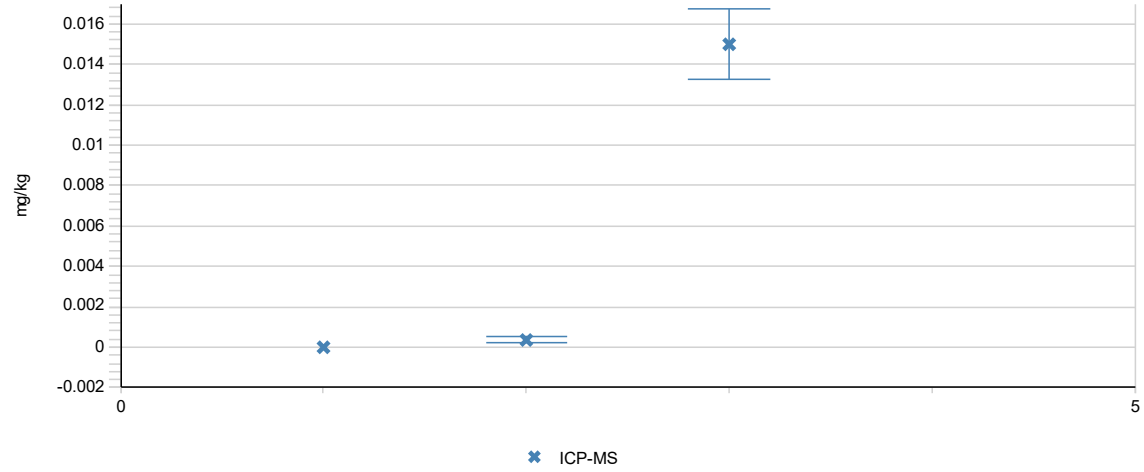

Measurand Cd Sample F6
10
5
0
-5
-10
mg/kg
0
5
ICP-MS


Measurand Cd
Sample F7
10
5
0
-5
-10
mg/kg
0
5
ICP-MS

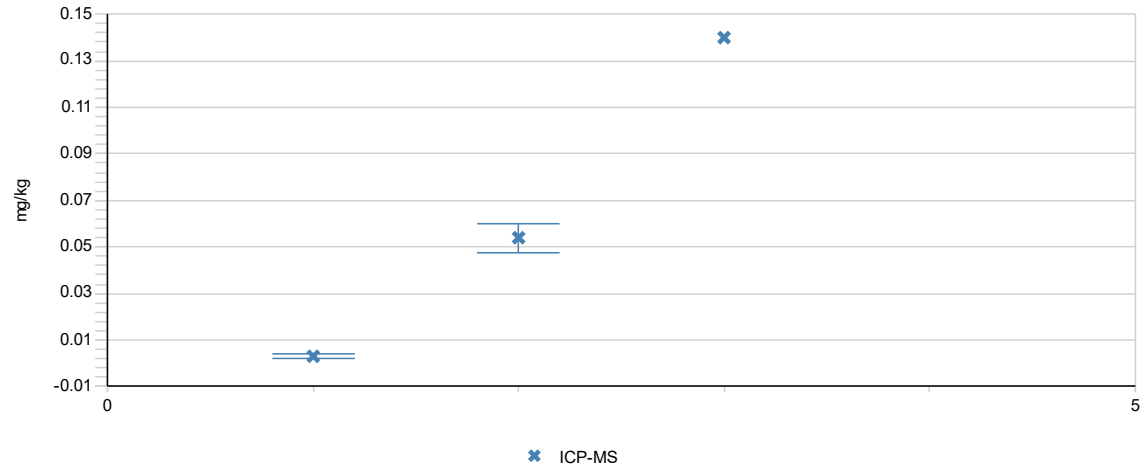

Measurand Cd
Sample LS_2lower
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
-0.002
mg/kg
0
5
ICP-MS


Measurand Cd
Sample LS_2upper
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
mg/kg
0
5
ICP-MS

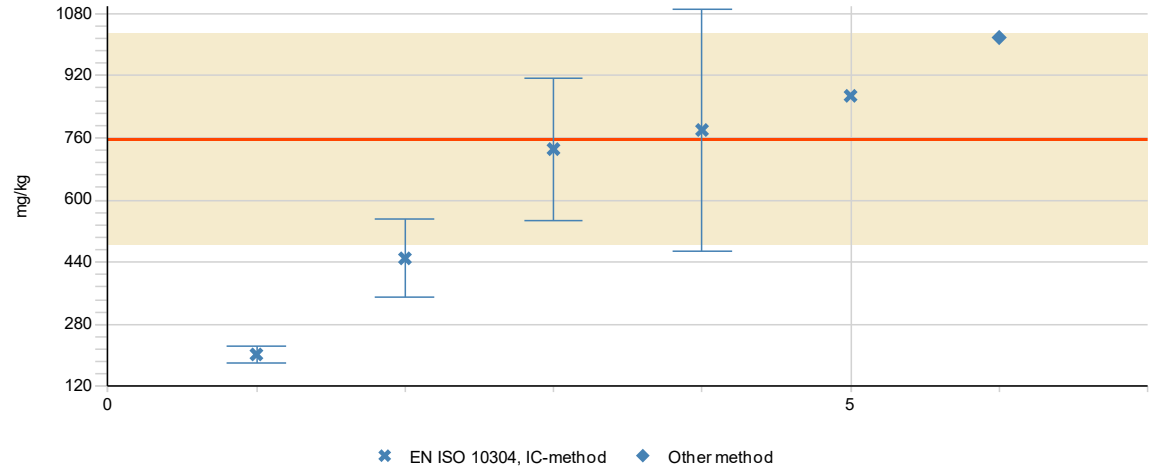
Measurand Cd Sample LS10lower



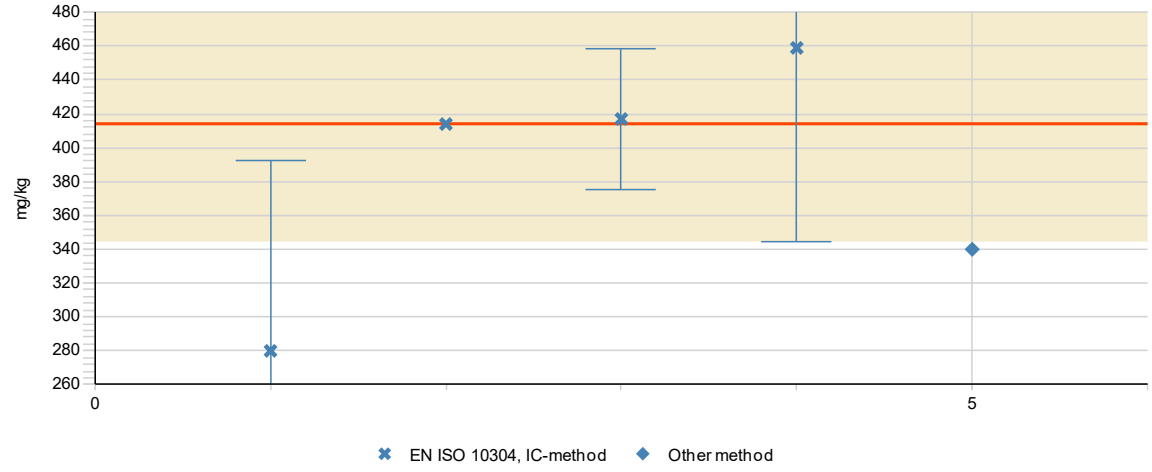

Measurand Cd Sample LS10upper



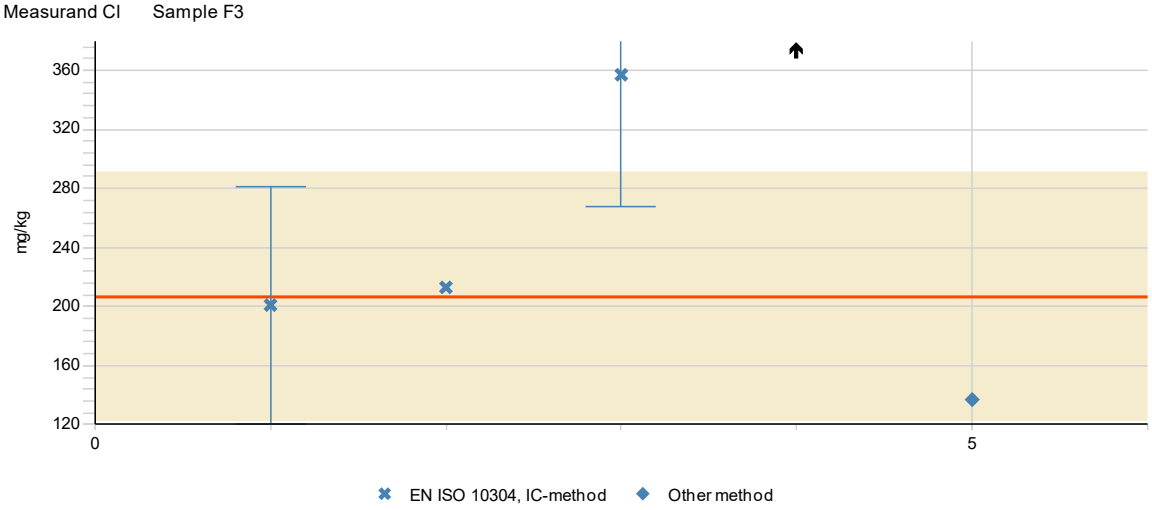

Measurand Cl Sample F1



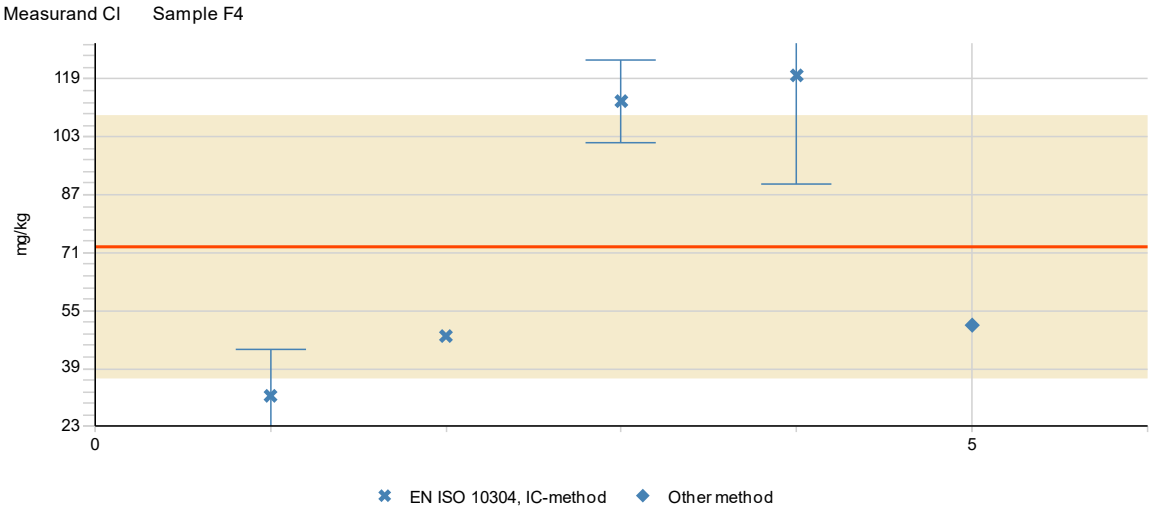
Measurand Cl Sample F2



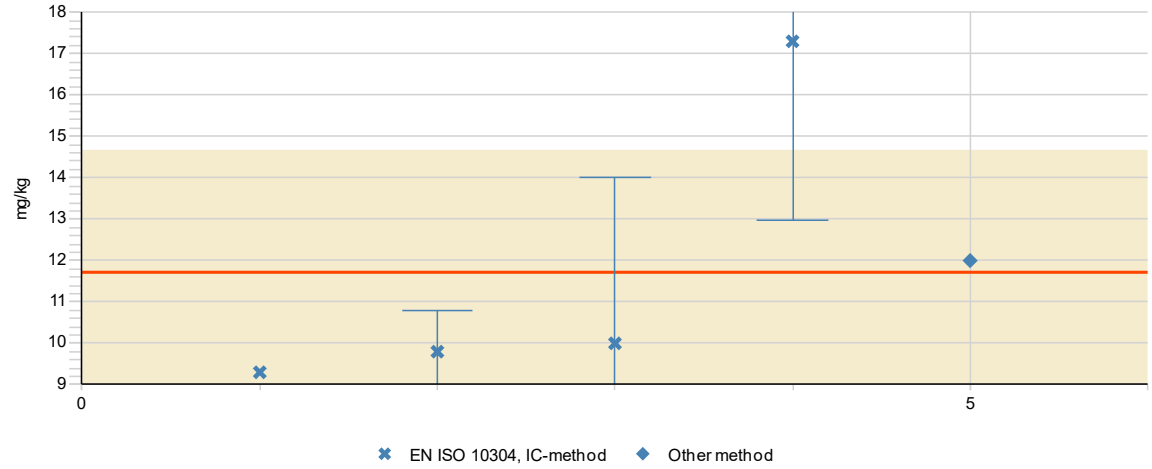

Measurand Cl Sample F3



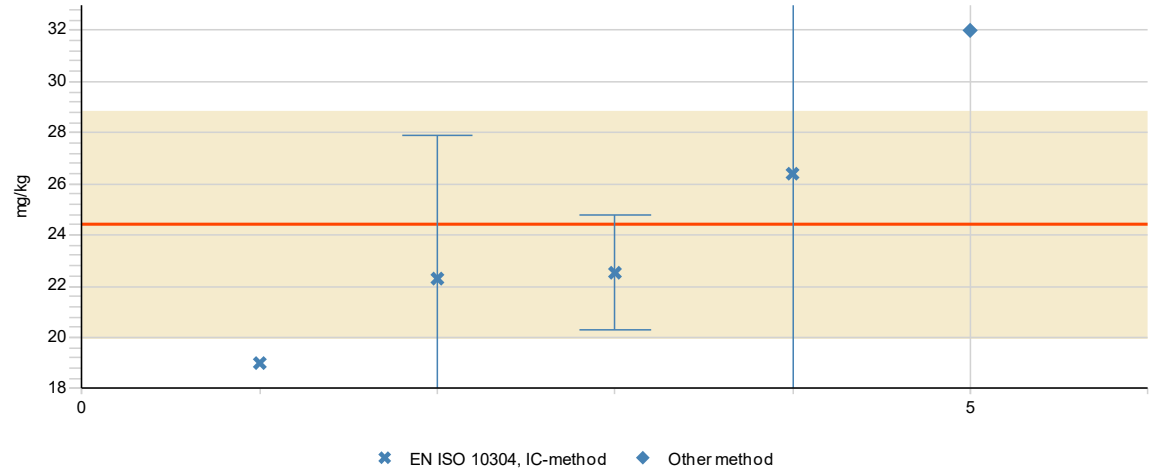

Measurand Cl Sample F4



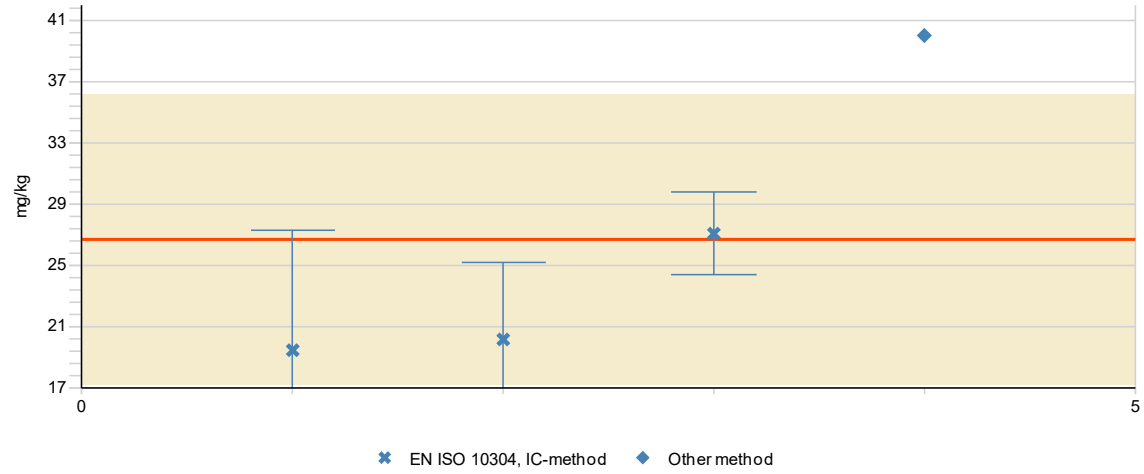
Measurand Cl Sample F5



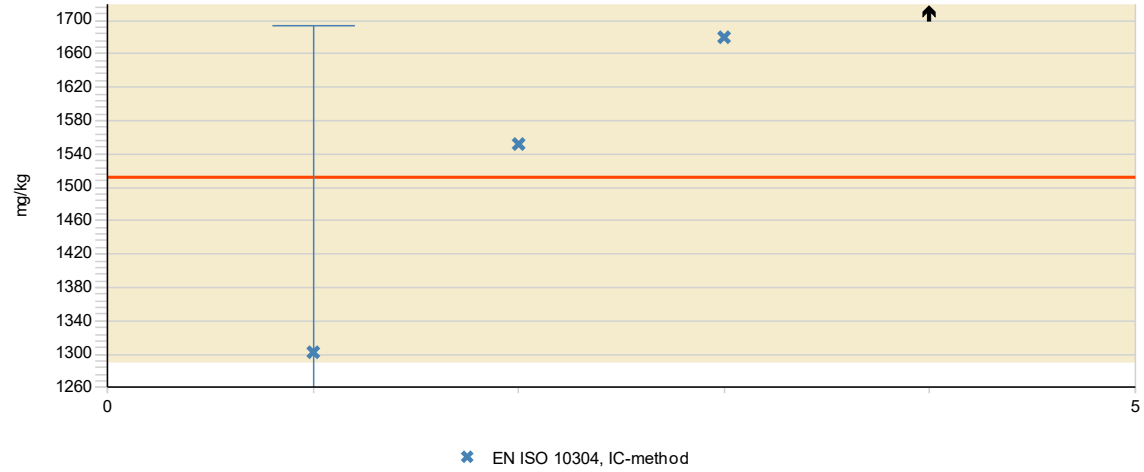

Measurand Cl Sample F6



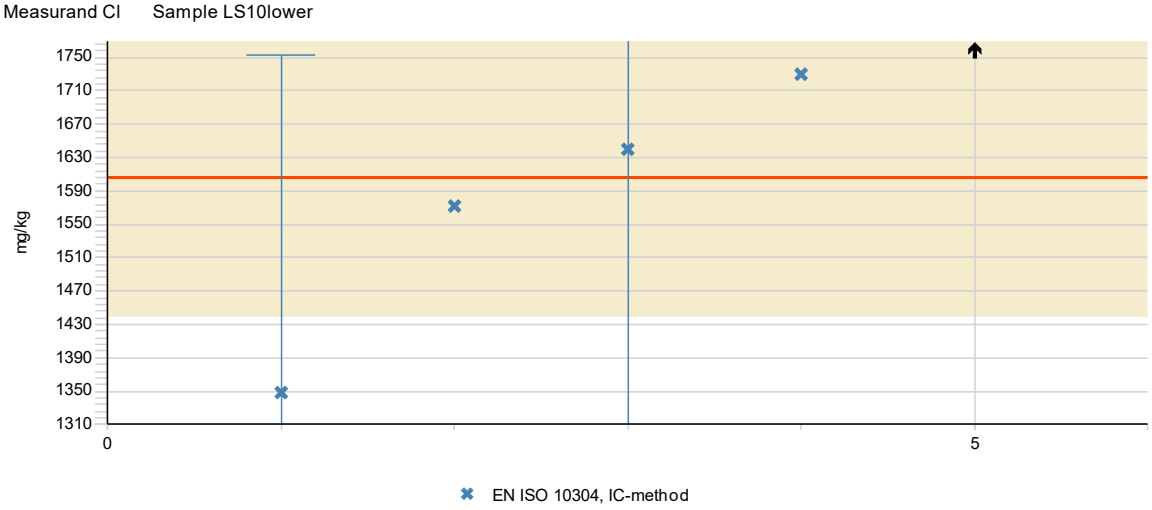

Measurand Cl Sample F7



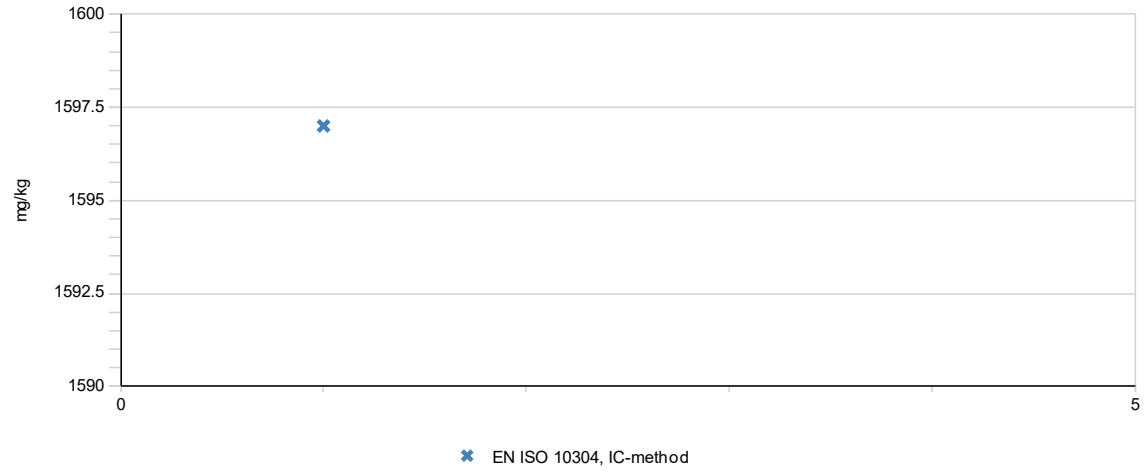
Measurand Cl Sample LS_2lower

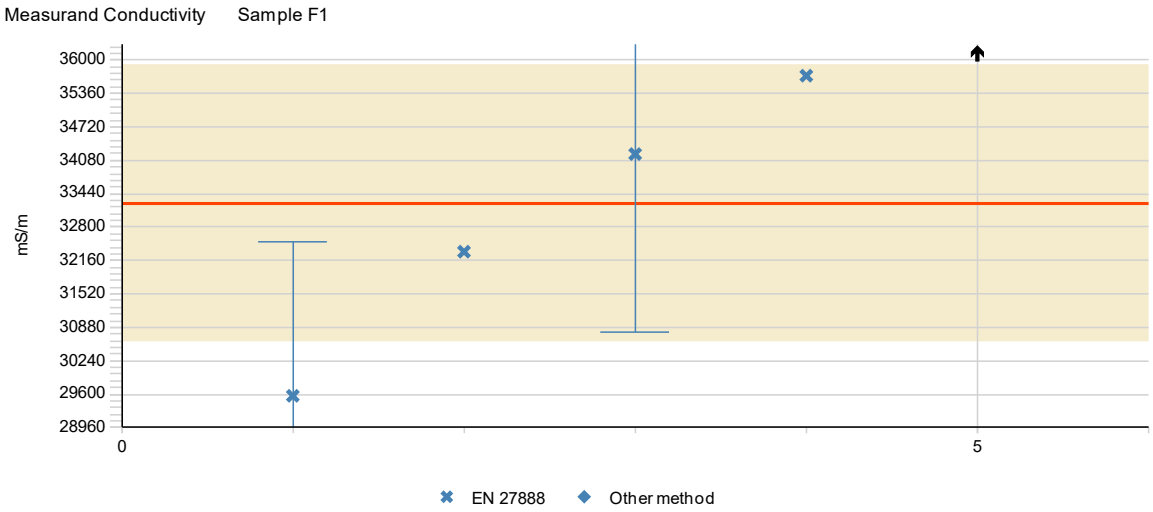


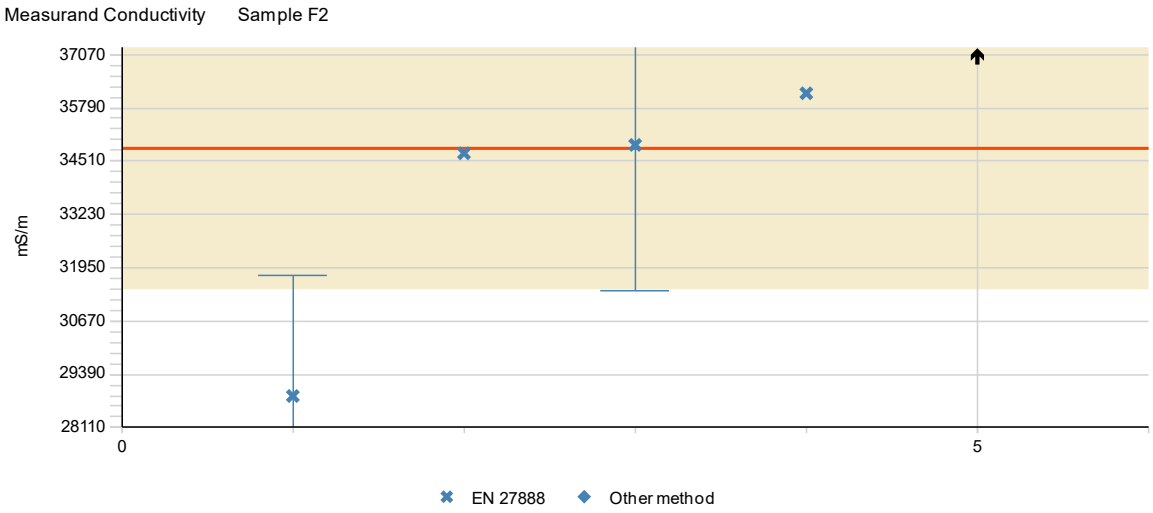

Measurand Cl Sample LS10lower

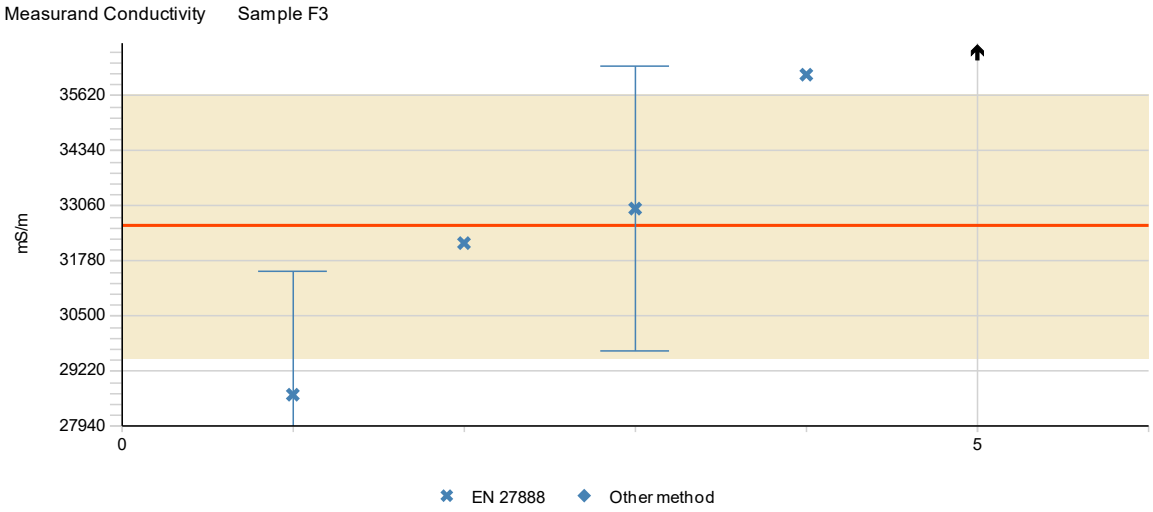


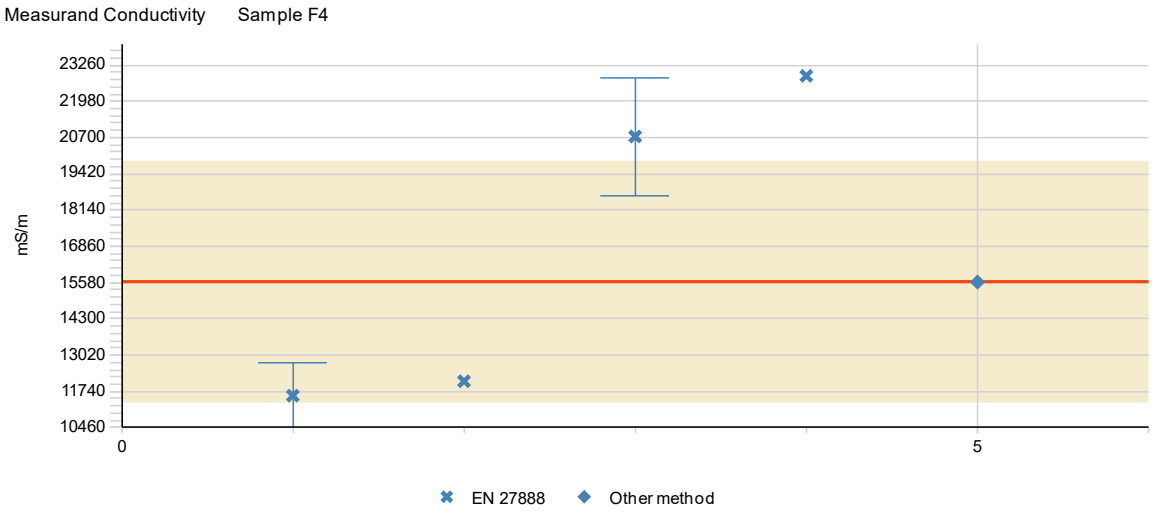

Measurand Cl Sample LS10upper

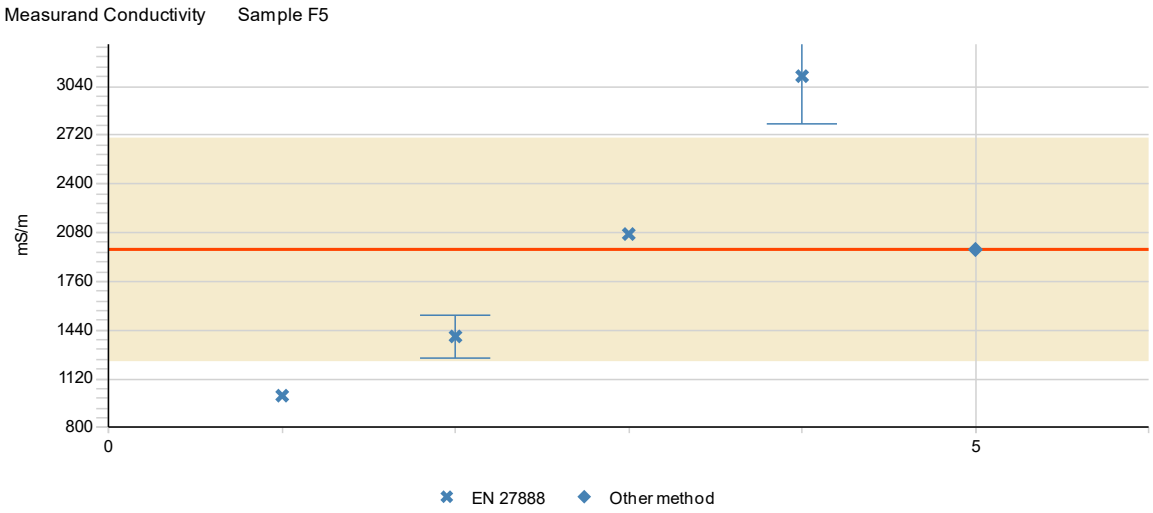


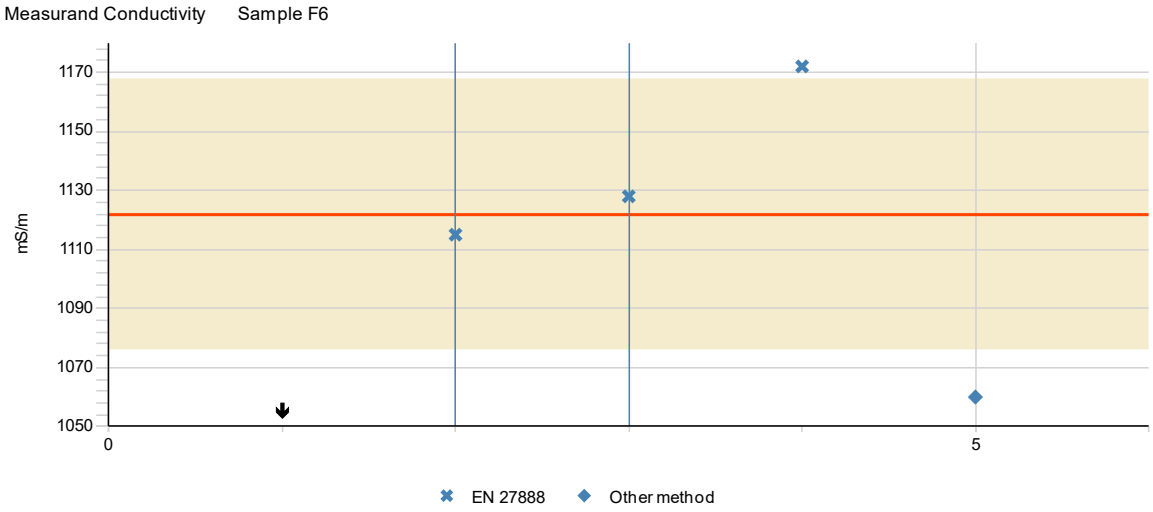

Measurand Conductivity Sample F1
36000
35360
34720
34080
33440
32800
32160
31520
30880
30240
29600
28960
mS/m
0
5
EN 27888
Other method


Measurand Conductivity Sample F2
37070
35790
34510
33230
31950
30670
29390
28110
mS/m
0
5
EN 27888
Other method

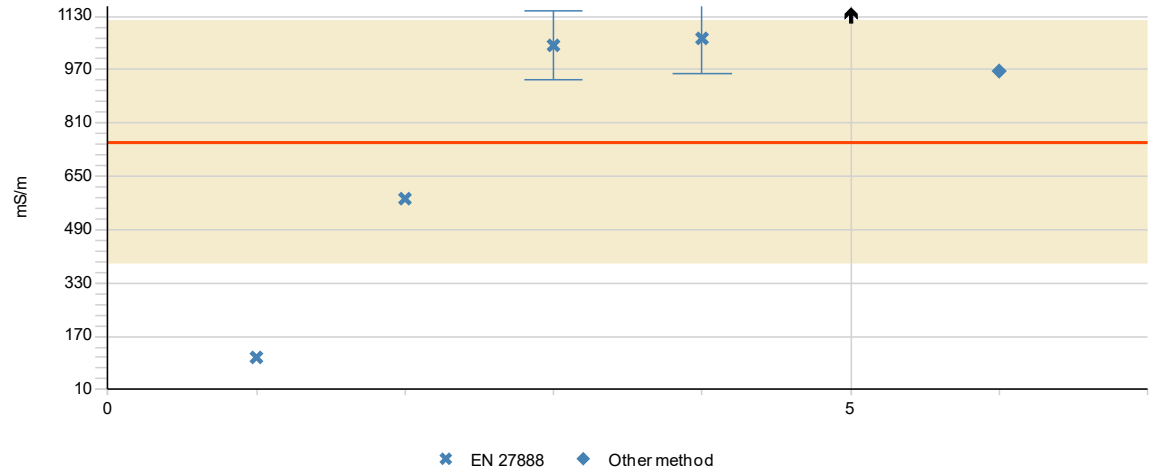

Measurand Conductivity Sample F3
35620
34340
33060
31780
30500
29220
27940
mS/m
0
5
EN 27888
Other method


Measurand Conductivity Sample F4
23260
21980
20700
19420
18140
16860
15580
14300
13020
11740
10460
mS/m
0
5
EN 27888
Other method

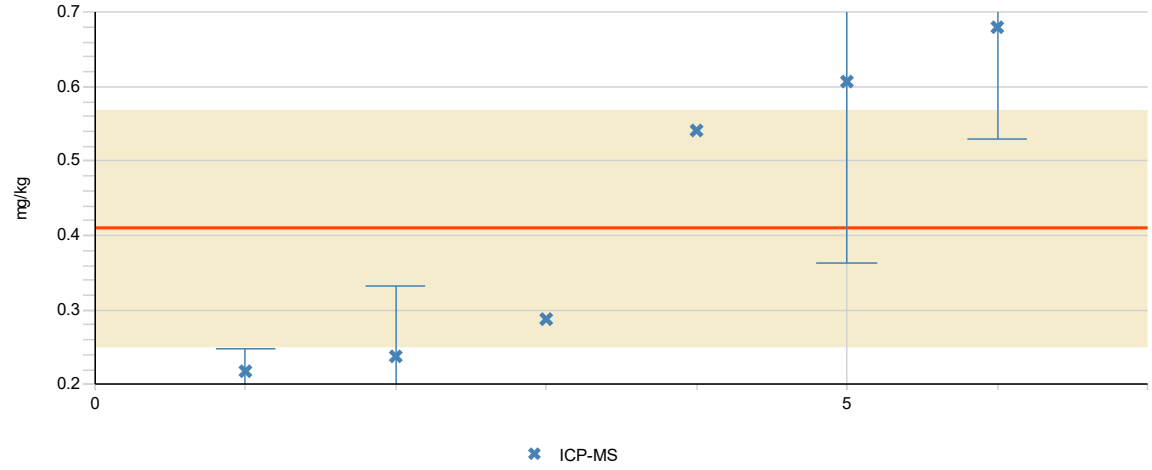

Measurand Conductivity Sample F5
3040
2720
2400
2080
1760
1440
1120
800
mS/m
0
5
EN 27888
Other method


Measurand Conductivity Sample F6
1170
1150
1130
1110
1090
1070
1050
mS/m
0
5
EN 27888
Other method

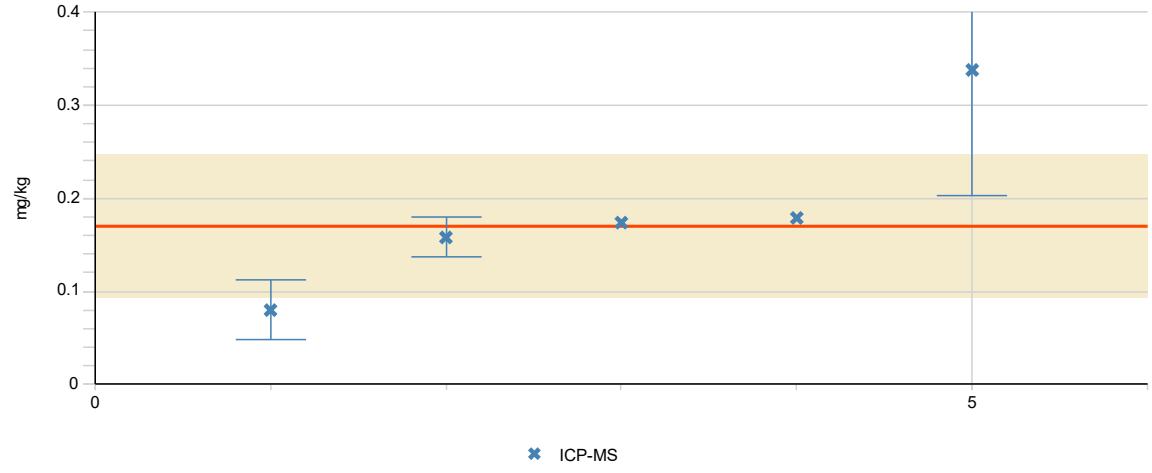
Measurand Conductivity Sample F7



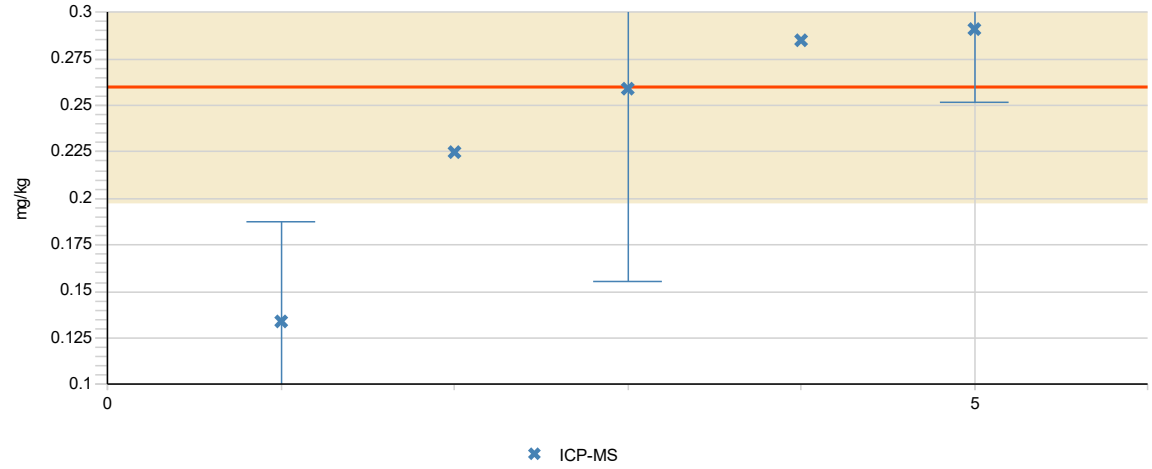

Measurand Cr Sample F1



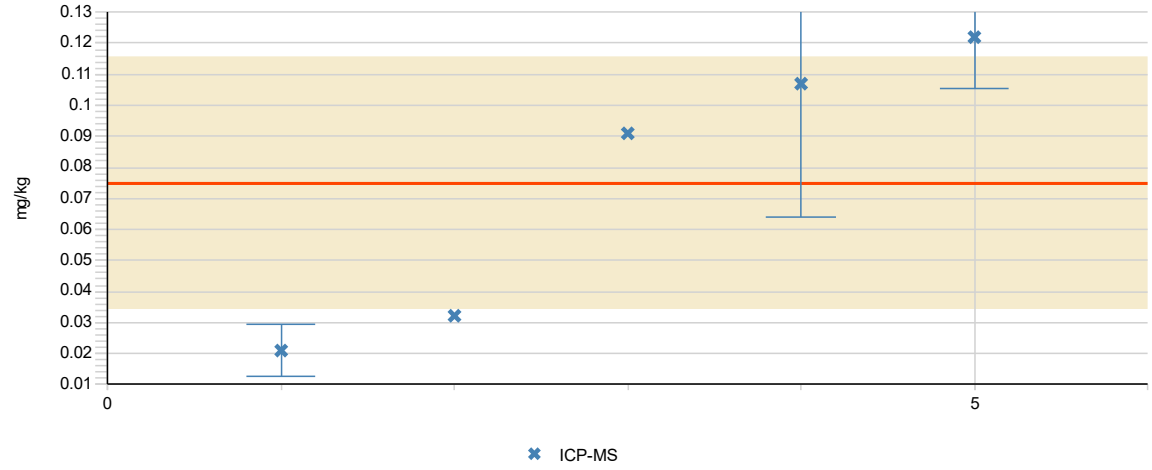

Measurand Cr Sample F2



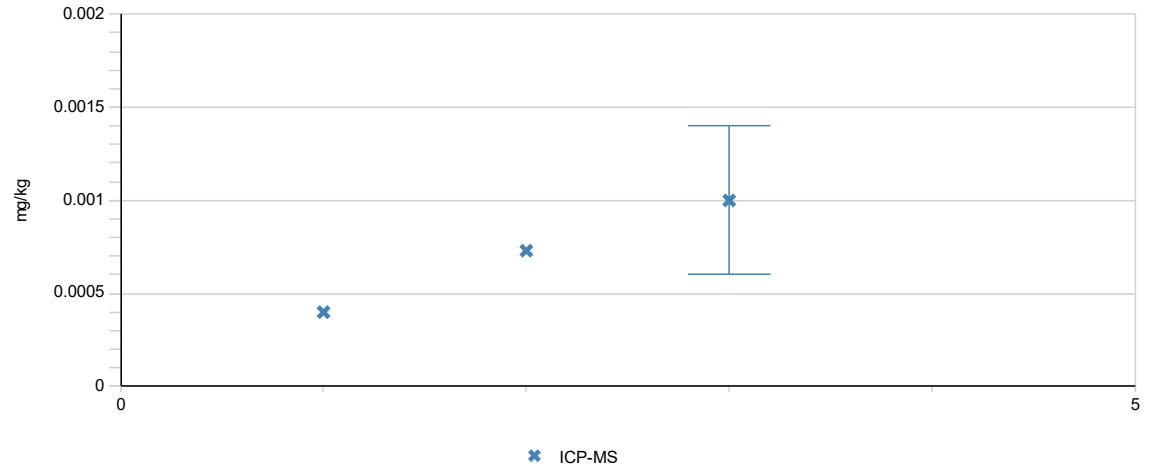
Measurand Cr Sample F3



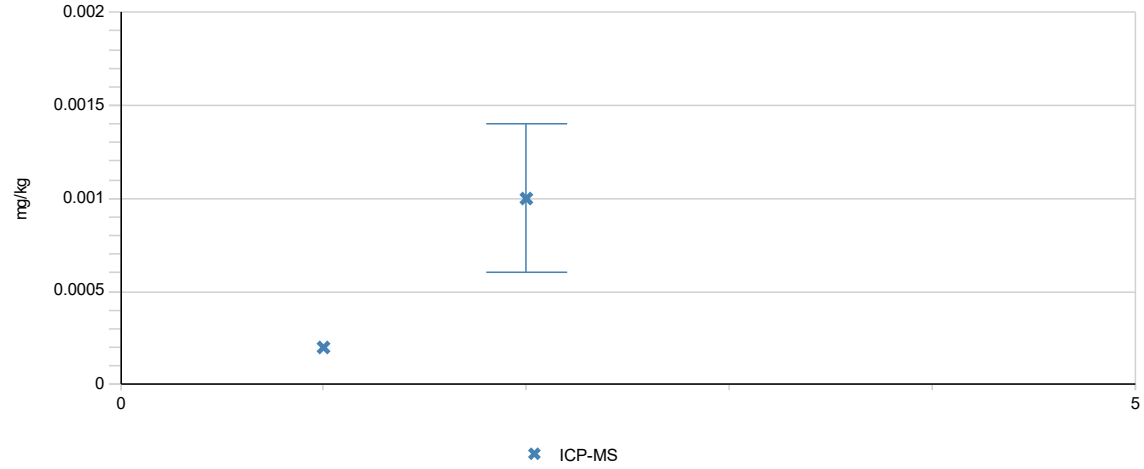

Measurand Cr Sample F4



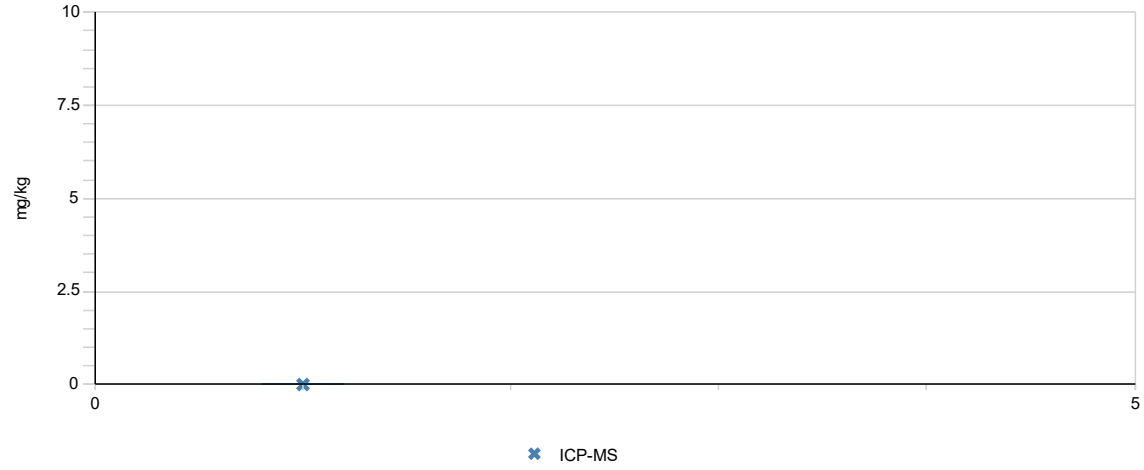

Measurand Cr Sample F5



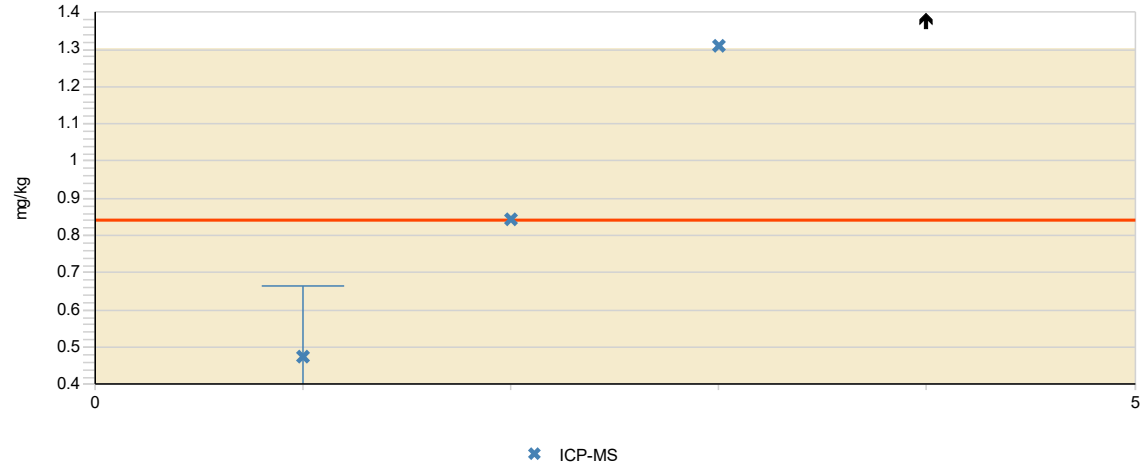
Measurand Cr Sample F6

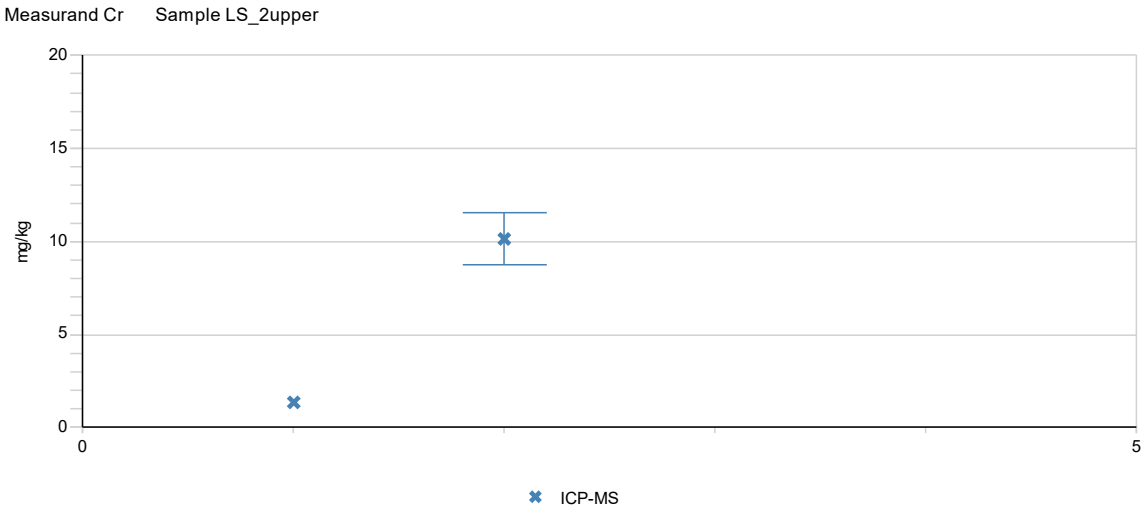


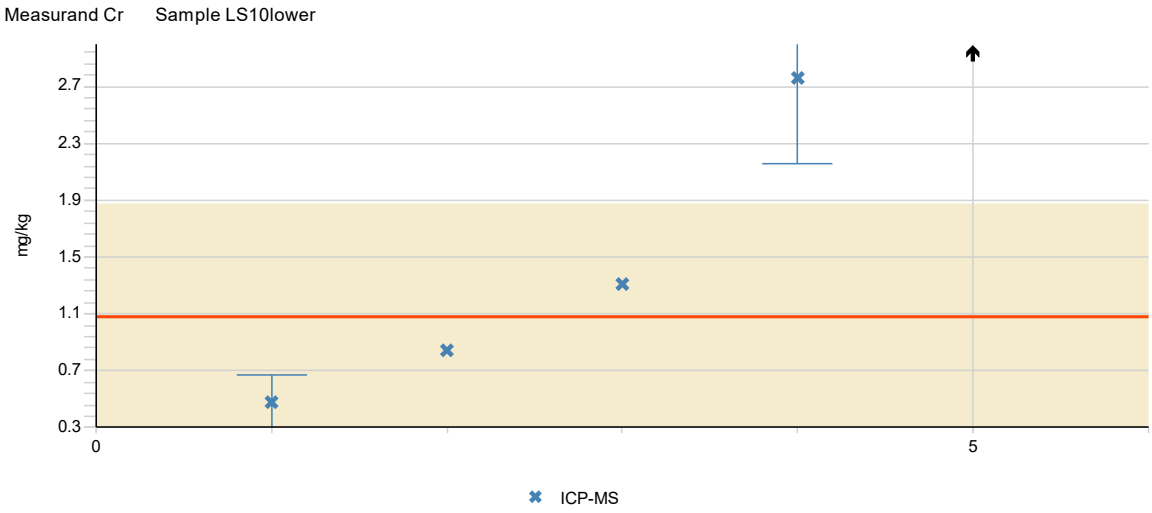

Measurand Cr Sample F7

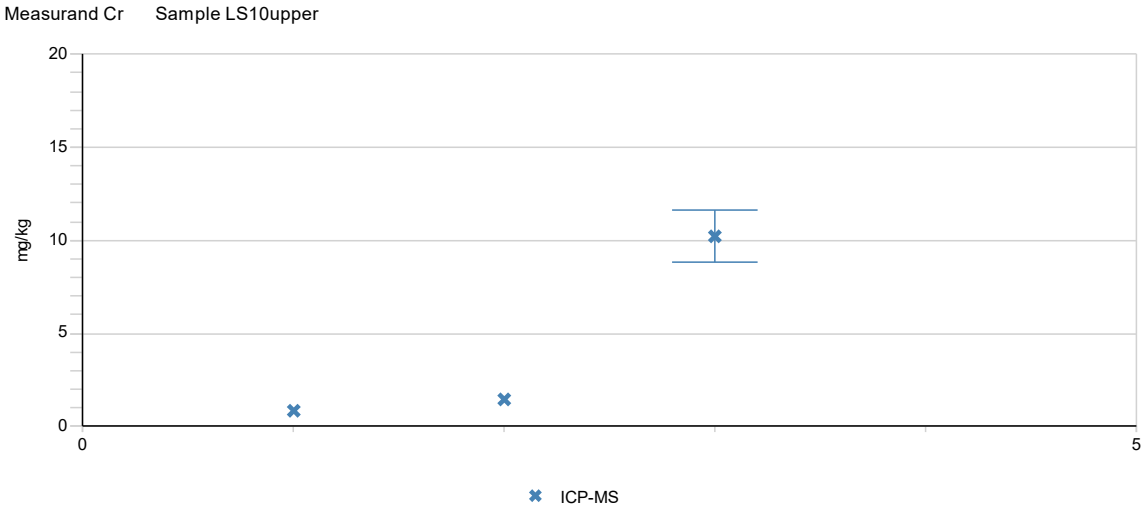



Measurand Cr Sample LS_2lower

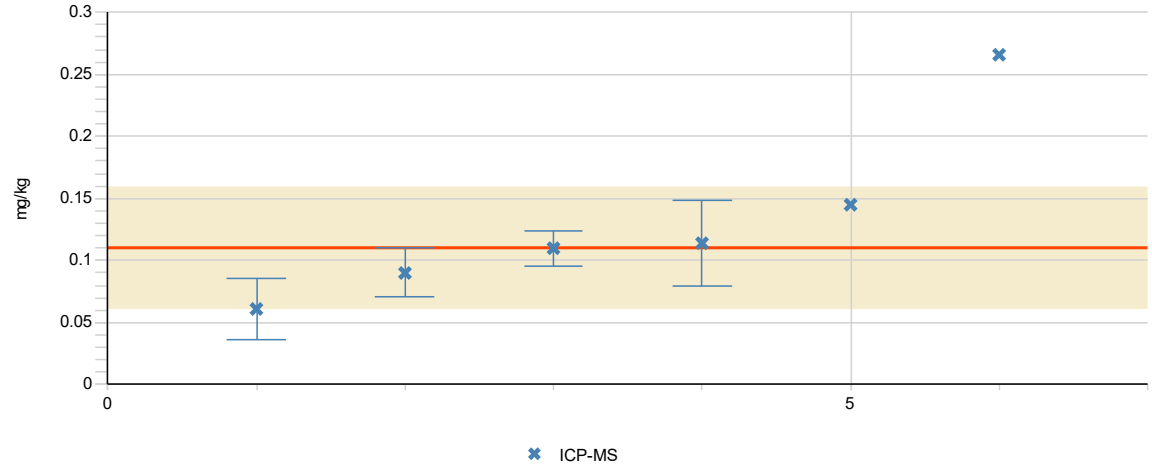



Measurand Cr
Sample LS_2upper
20
15
10
5
0
mg/kg
0
5
ICP-MS

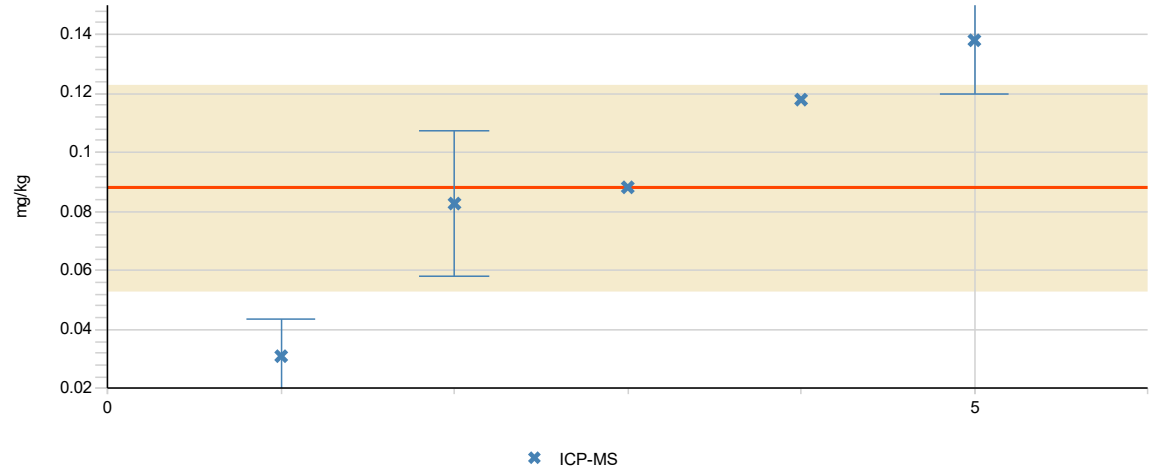

Measurand Cr
Sample LS10lower
2.7
2.3
1.9
1.5
1.1
0.7
0.3
mg/kg
0
5
ICP-MS


Measurand Cr
Sample LS10upper
20
15
10
5
0
mg/kg
0
5
ICP-MS

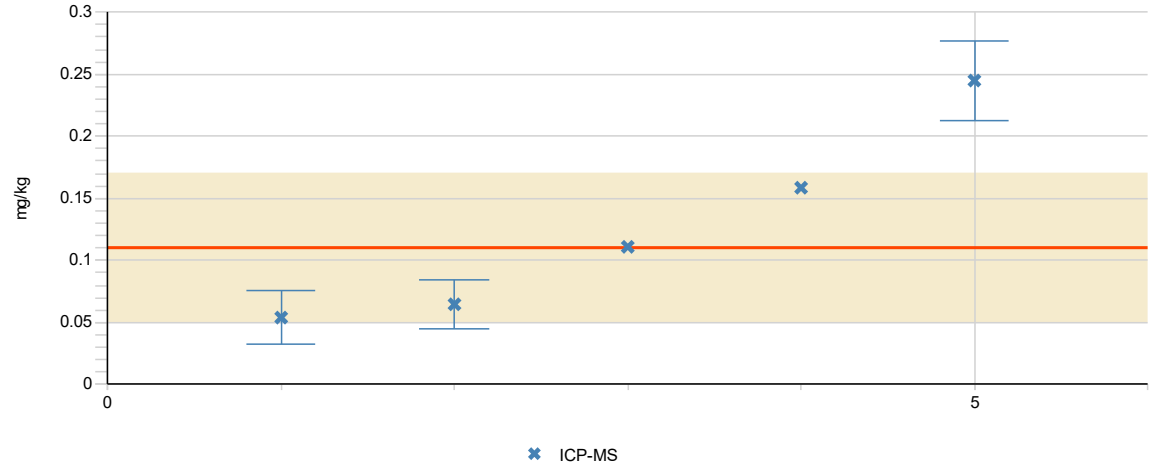
Measurand Cu Sample F1

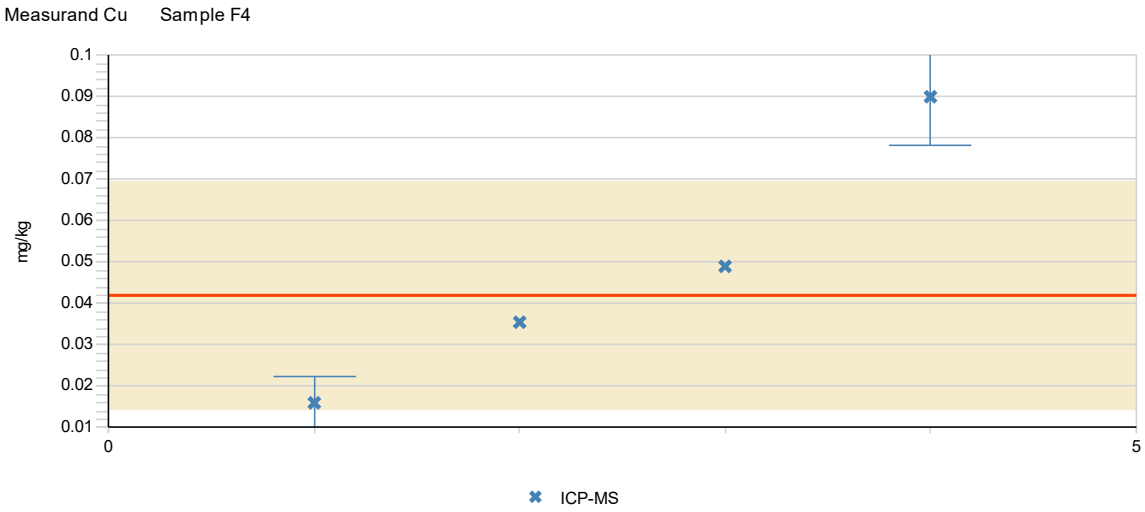


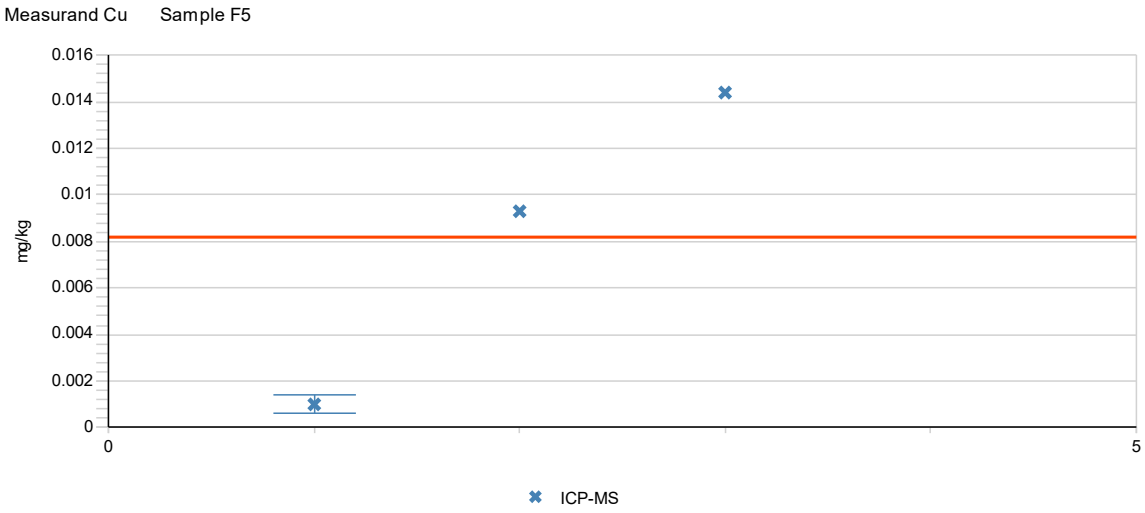

Measurand Cu Sample F2

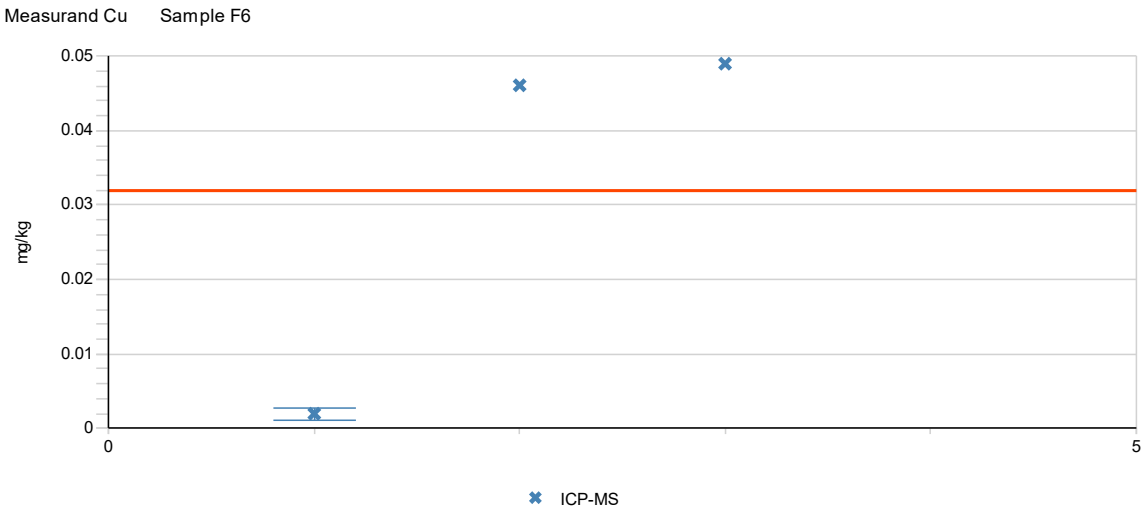



Measurand Cu Sample F3

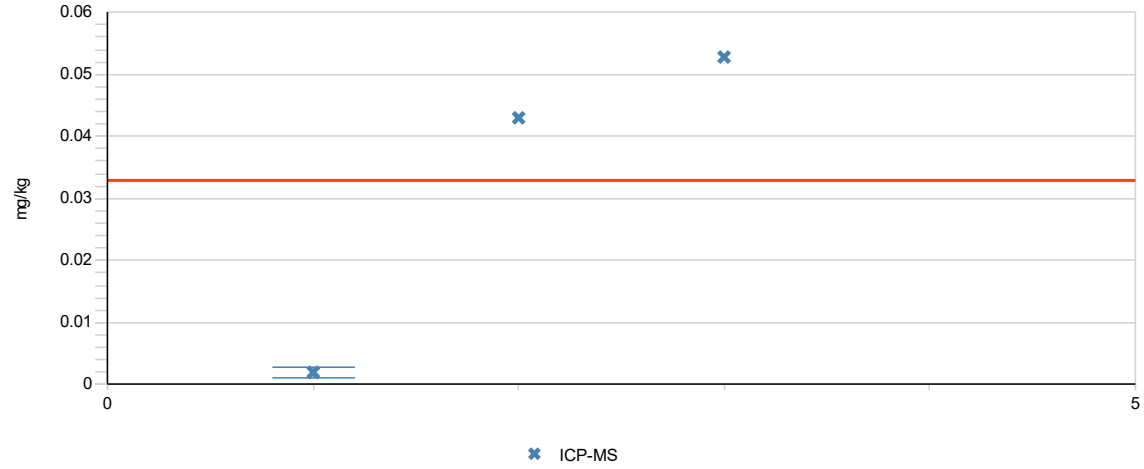



Measurand Cu Sample F4
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
mg/kg
0
5
ICP-MS

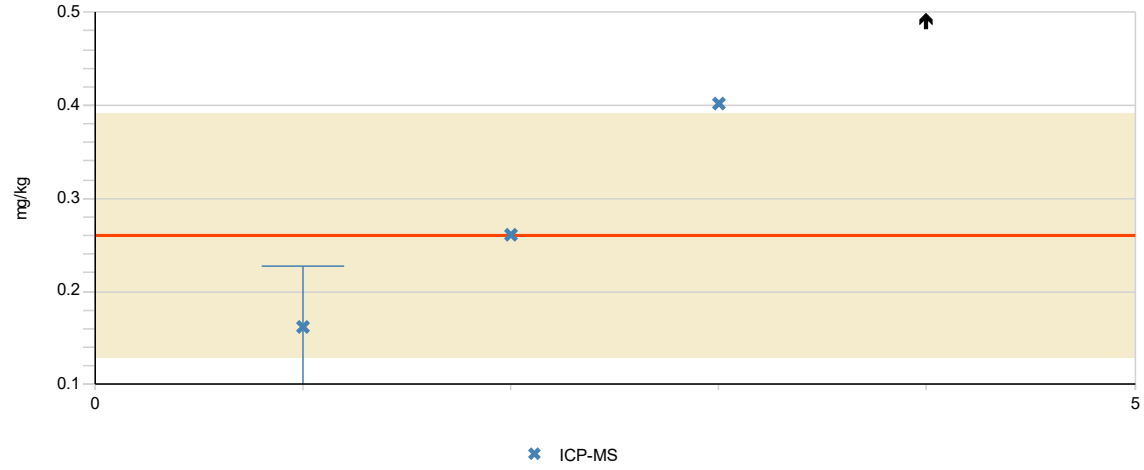

Measurand Cu Sample F5
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
mg/kg
0
5
ICP-MS


Measurand Cu Sample F6
0.05
0.04
0.03
0.02
0.01
0
mg/kg
0
5
ICP-MS

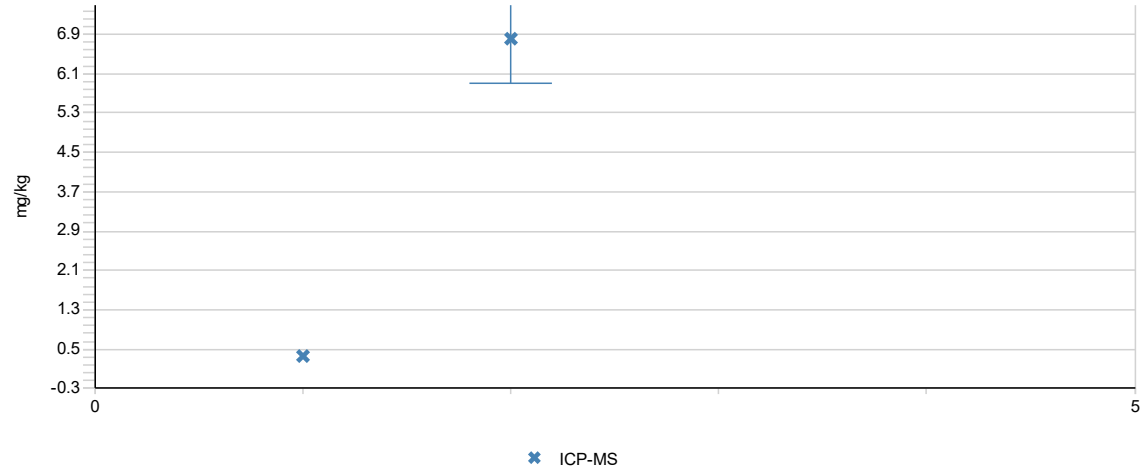
Measurand Cu Sample F7



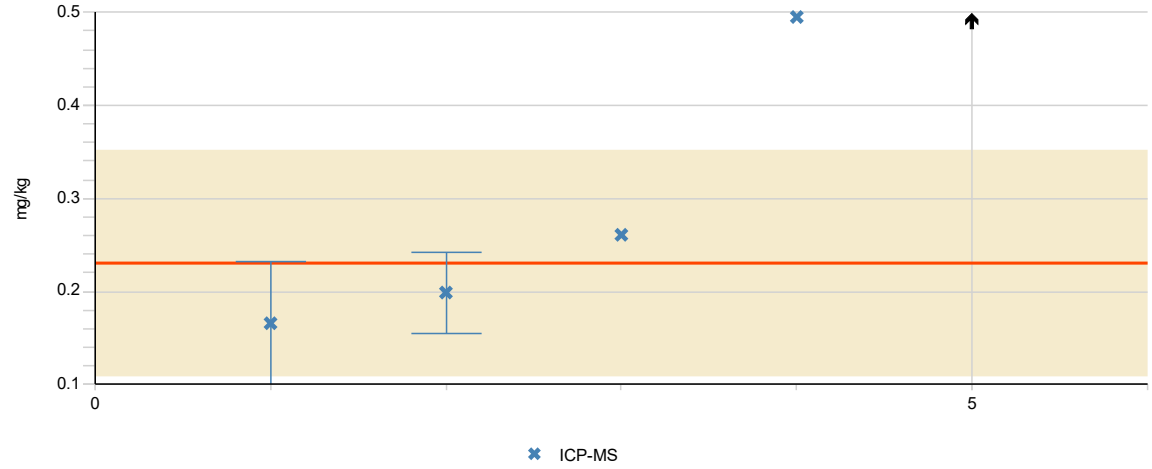

Measurand Cu Sample LS_2lower



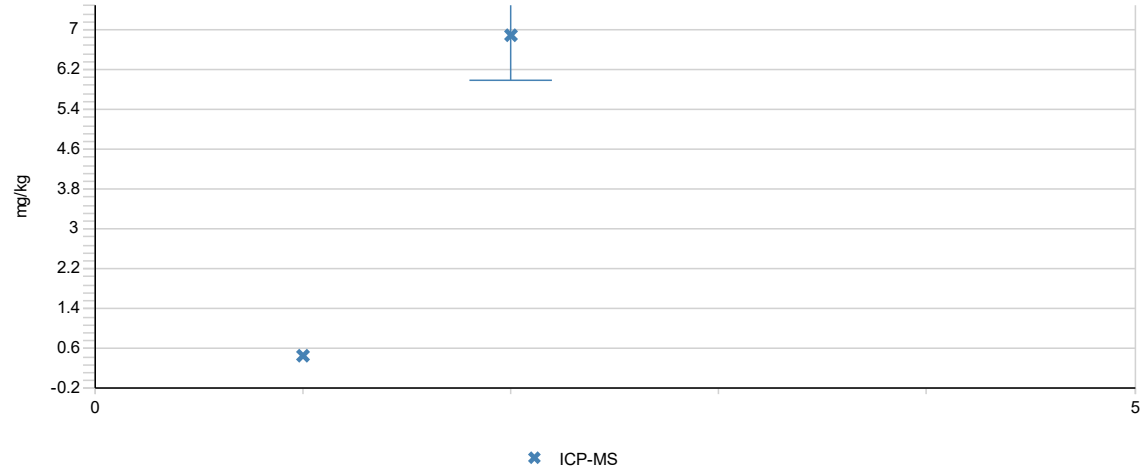

Measurand Cu Sample LS_2upper



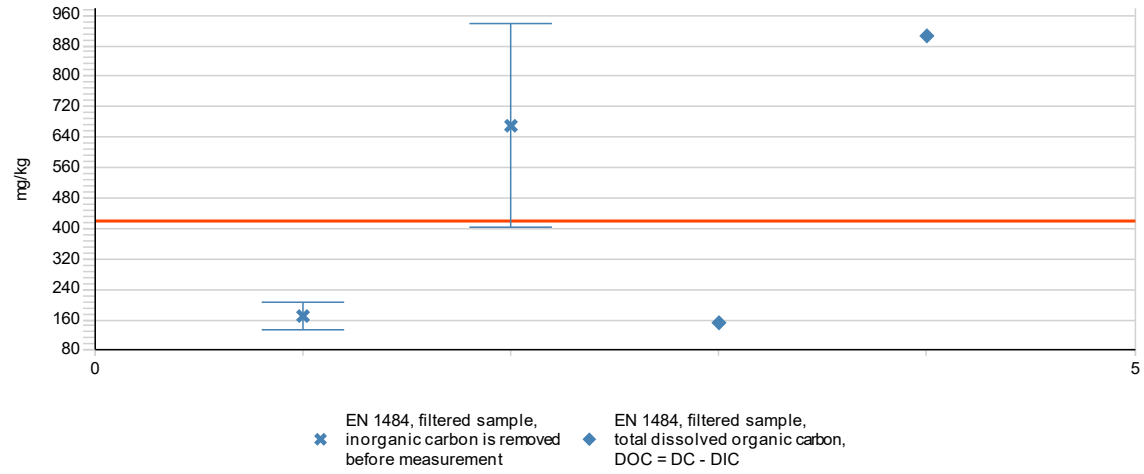
Measurand Cu Sample LS10lower



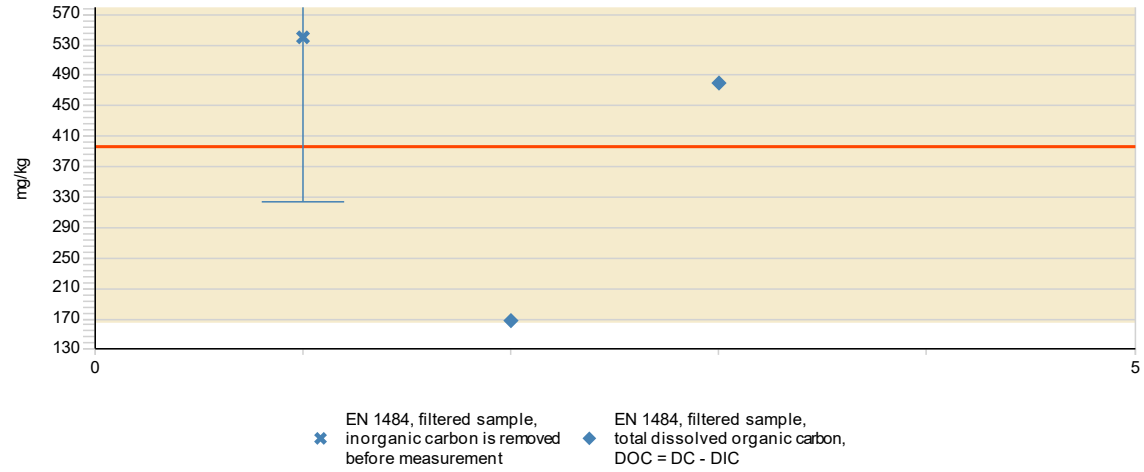

Measurand Cu Sample LS10upper



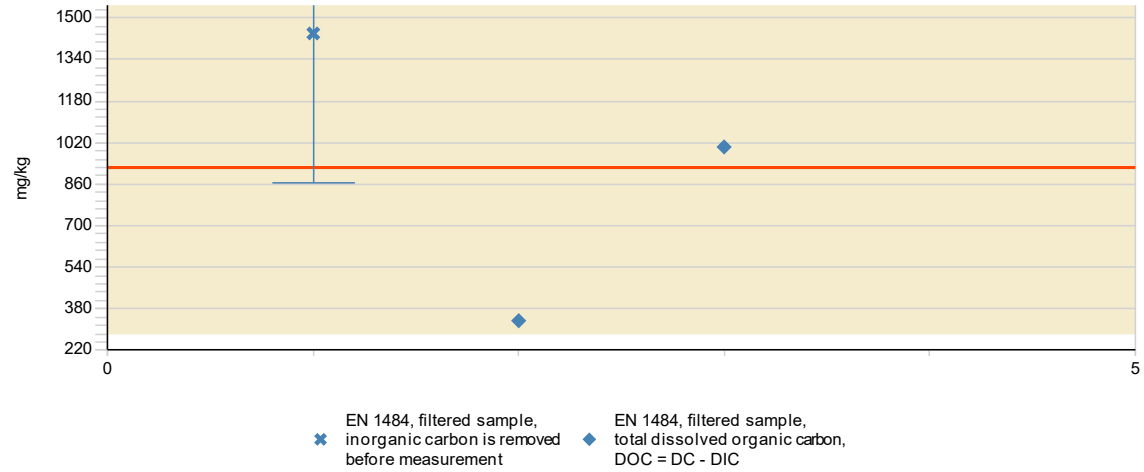

Measurand DOC Sample F1



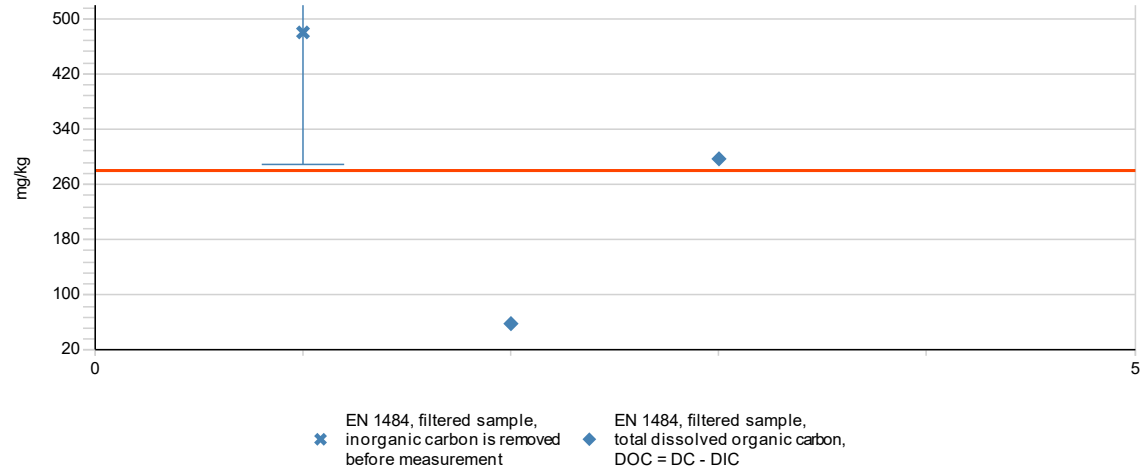
Measurand DOC Sample F2



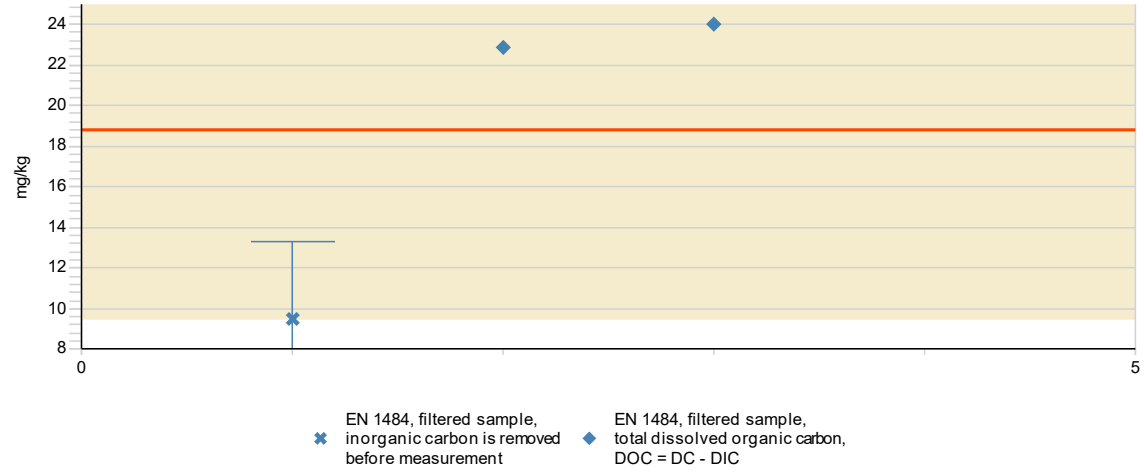

Measurand DOC Sample F3



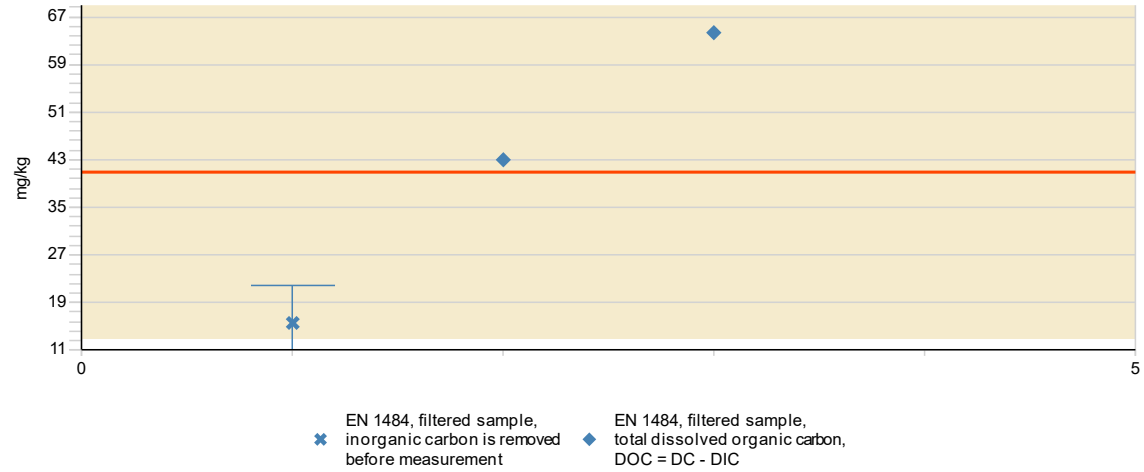

Measurand DOC Sample F4



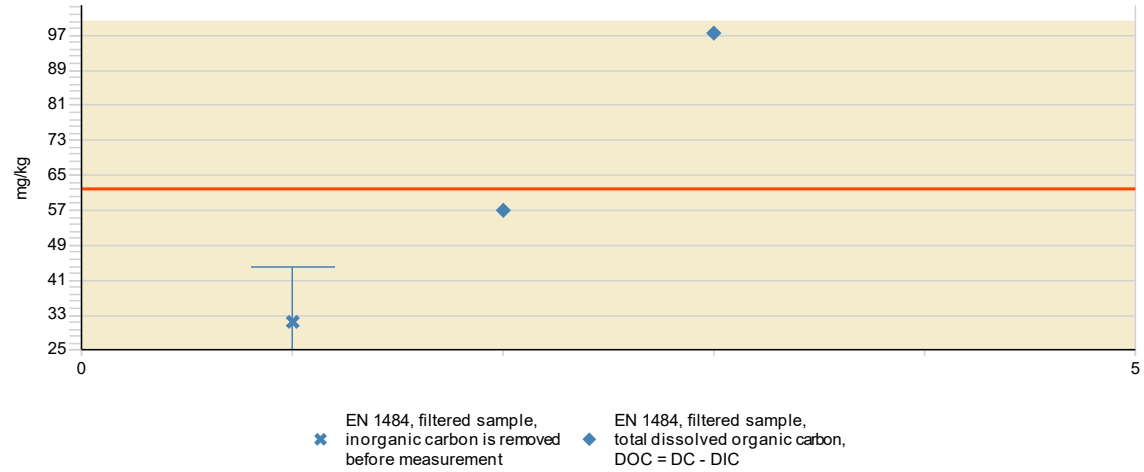
Measurand DOC Sample F5



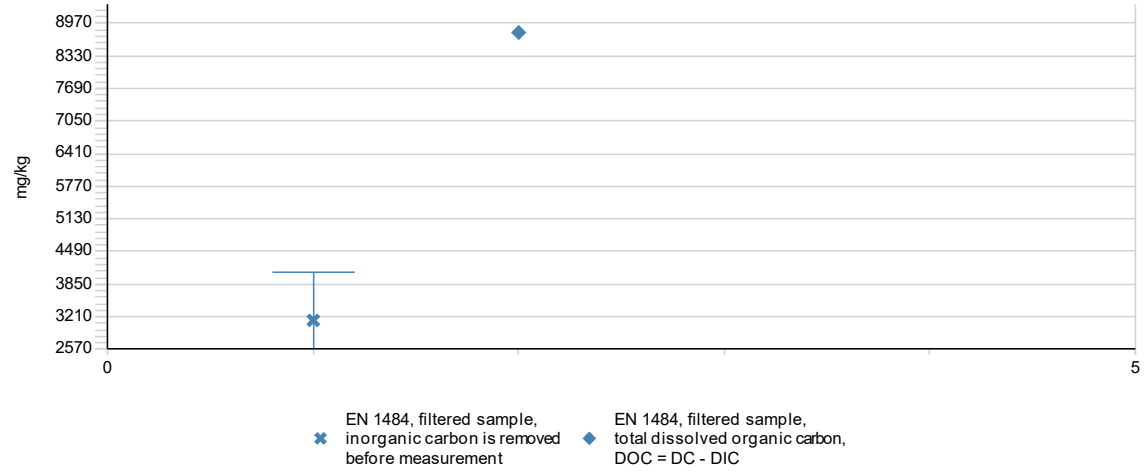

Measurand DOC Sample F6



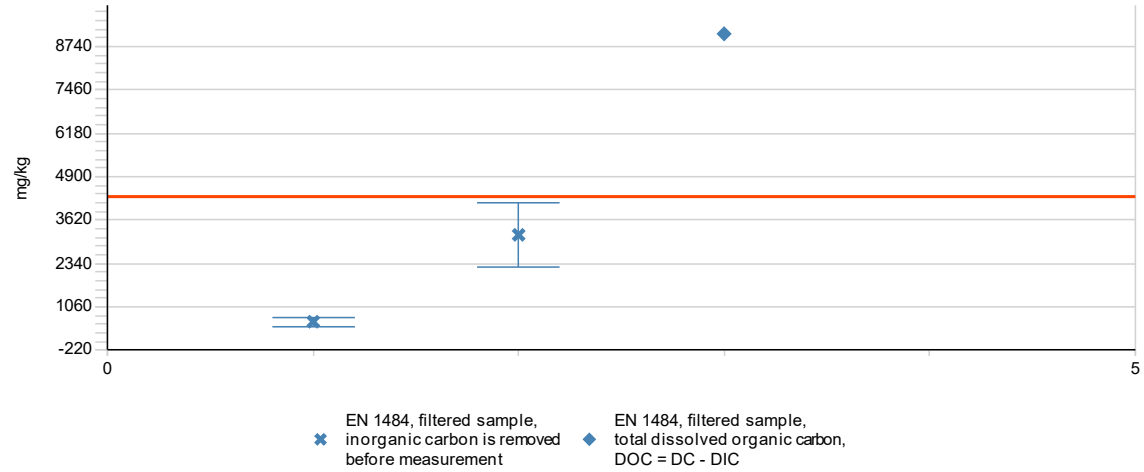

Measurand DOC Sample F7



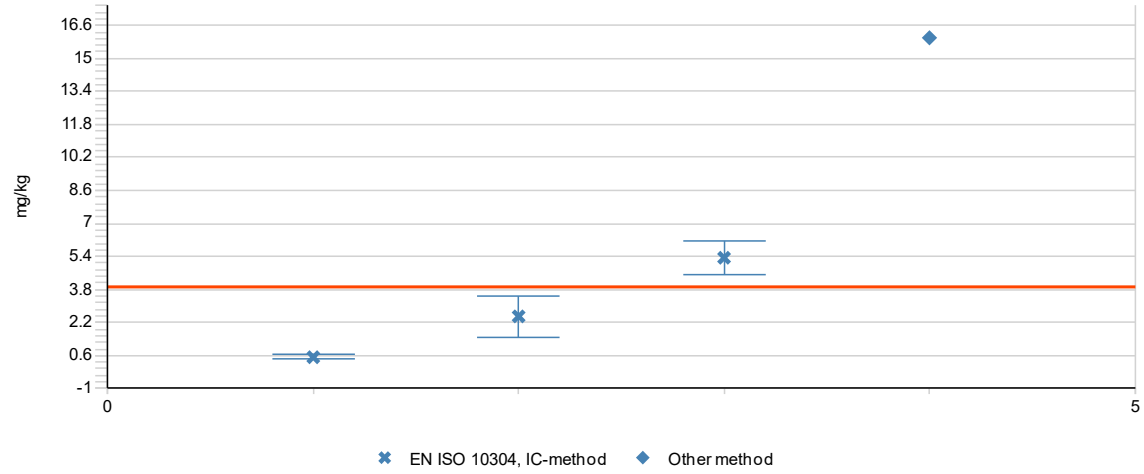
Measurand DOC Sample LS_2lower

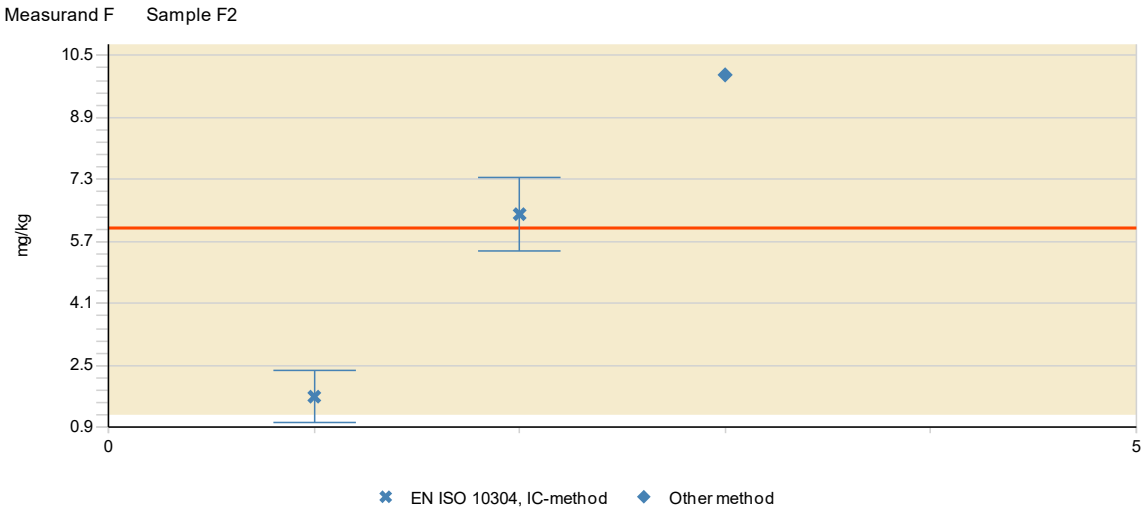


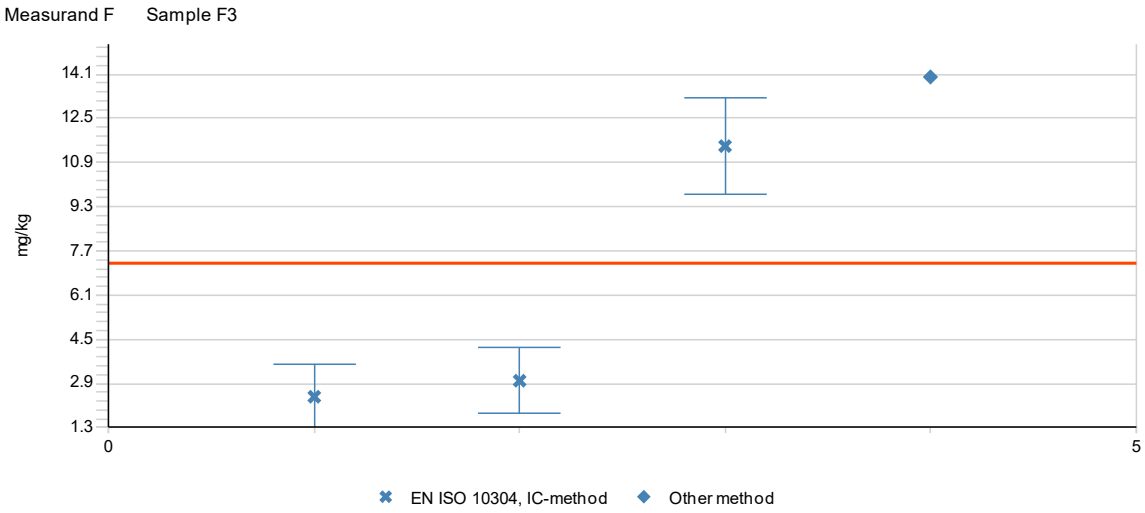

Measurand DOC Sample LS10lower

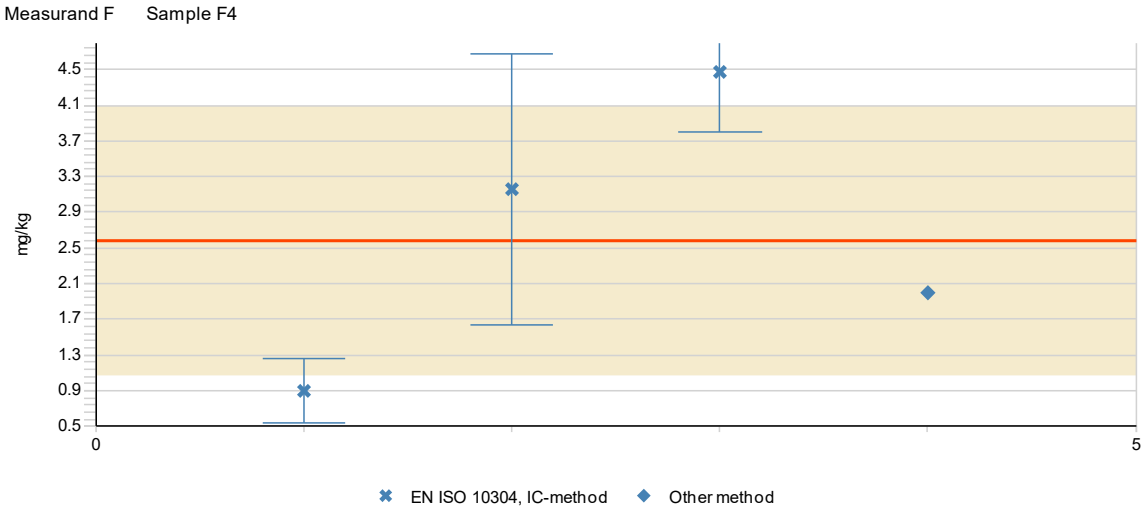



Measurand F Sample F1

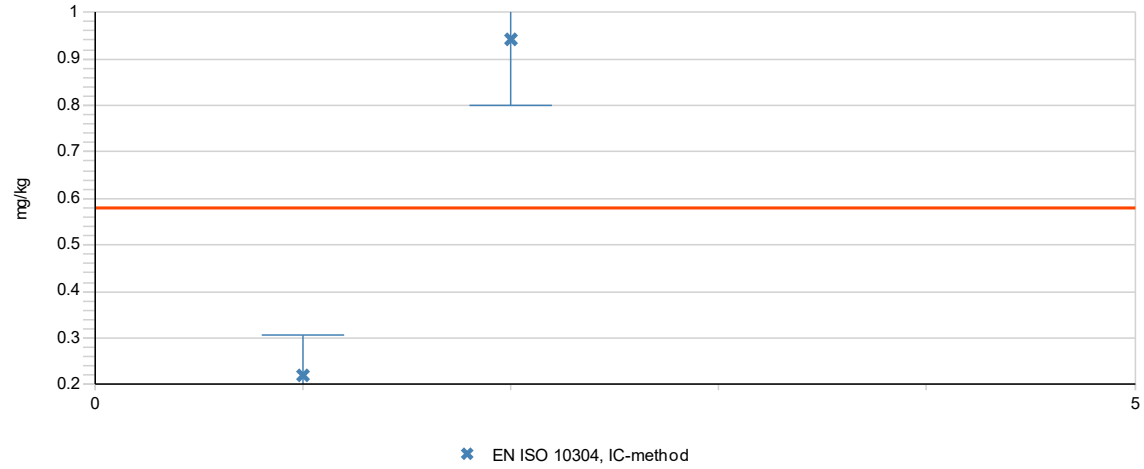



Measurand F Sample F2
10.5
8.9
7.3
5.7
4.1
2.5
0.9
mg/kg
0
5
EN ISO 10304, IC-method
Other method

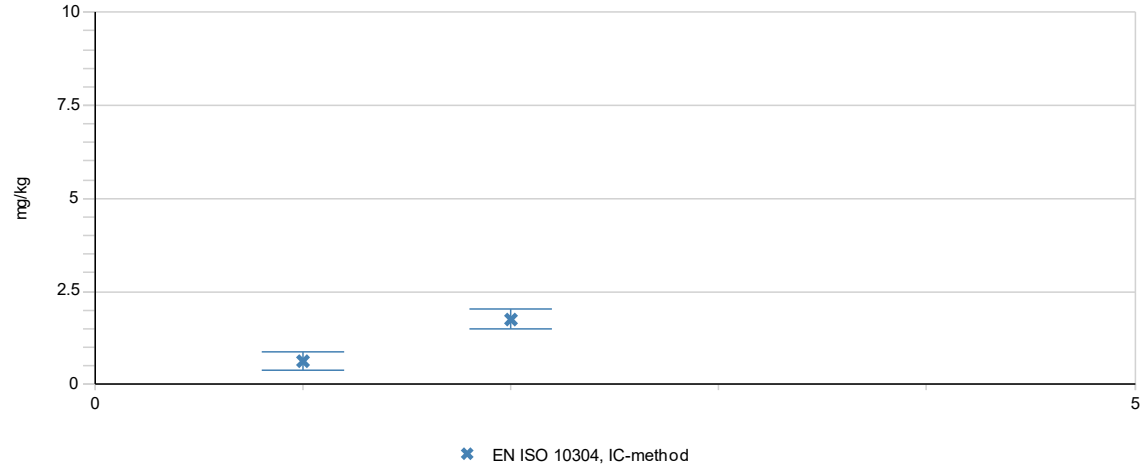

Measurand F Sample F3
14.1
12.5
10.9
9.3
7.7
6.1
4.5
2.9
1.3
mg/kg
0
5
EN ISO 10304, IC-method
Other method


Measurand F Sample F4
4.5
4.1
3.7
3.3
2.9
2.5
2.1
1.7
1.3
0.9
0.5
mg/kg
0
5
EN ISO 10304, IC-method
Other method

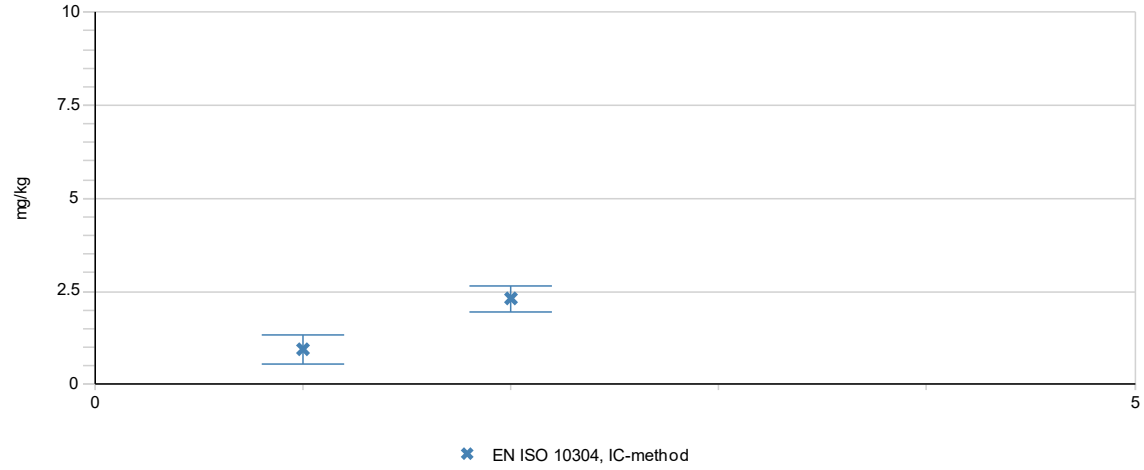
Measurand F Sample F5

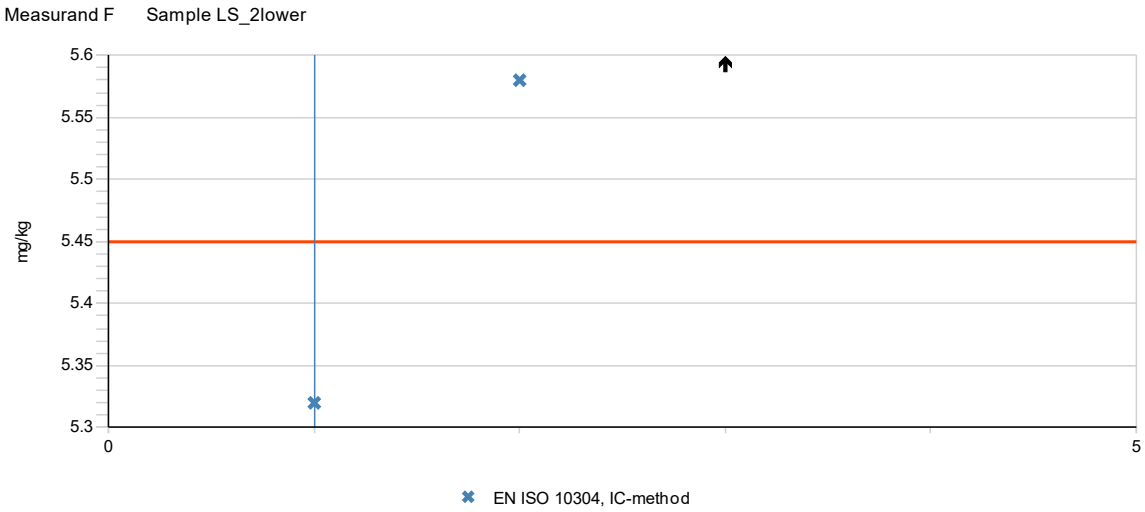


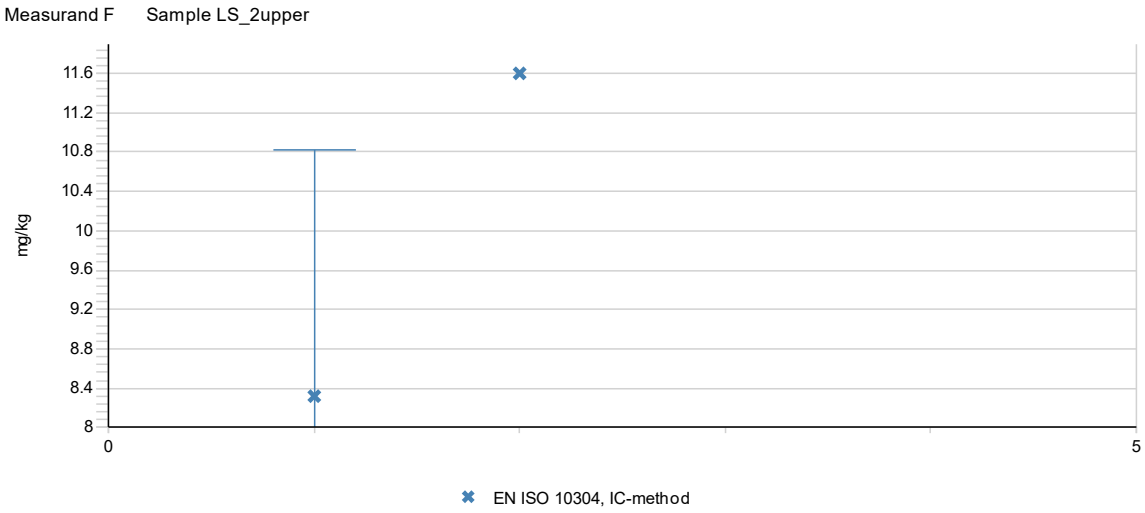

Measurand F Sample F6

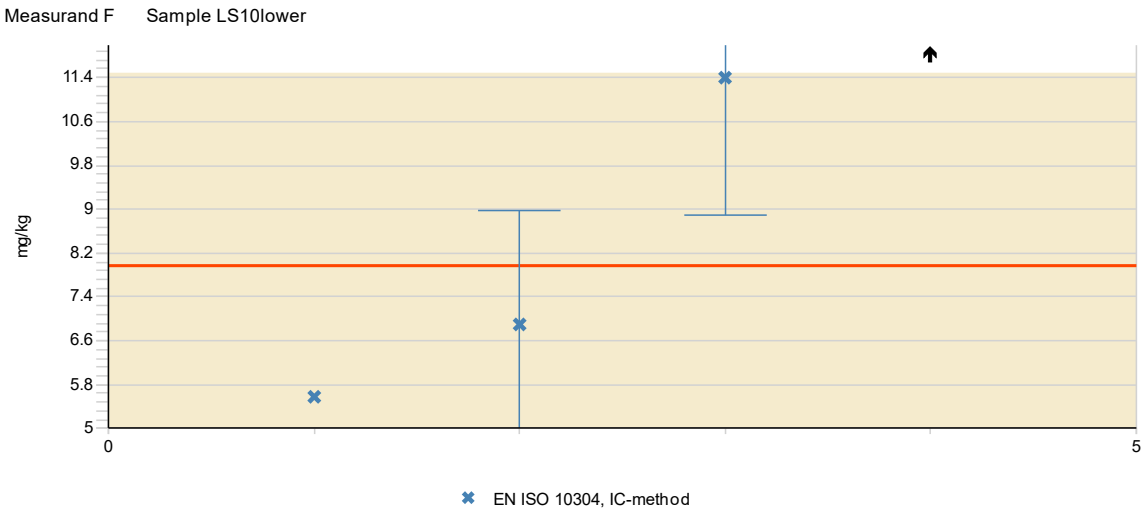



Measurand F Sample F7

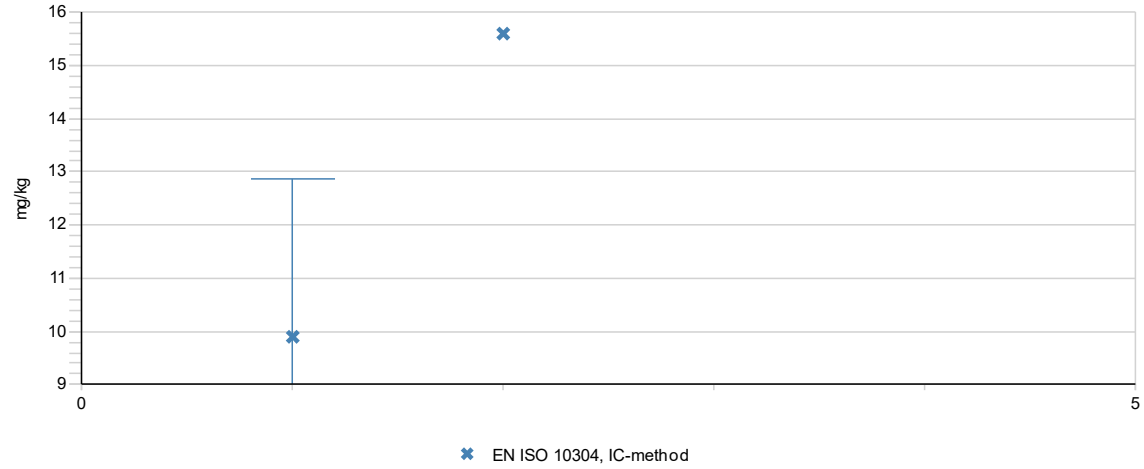



Measurand F
Sample LS_2lower
mg/kg
5.6
5.55
5.5
5.45
5.4
5.35
5.3
0
5
EN ISO 10304, IC-method

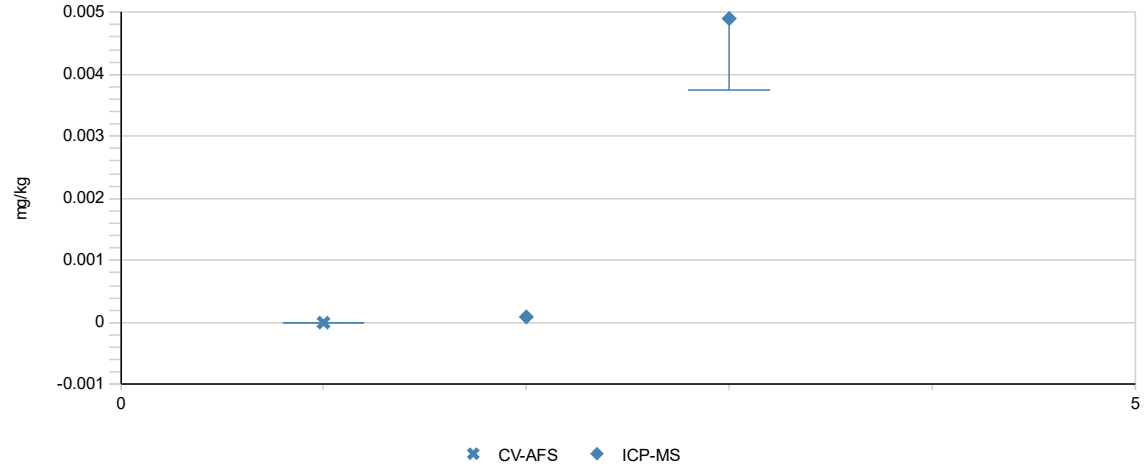

Measurand F
Sample LS_2upper
mg/kg
11.6
11.2
10.8
10.4
10
9.6
9.2
8.8
8.4
8
0
5
EN ISO 10304, IC-method


Measurand F
Sample LS10lower
mg/kg
11.4
10.6
9.8
9
8.2
7.4
6.6
5.8
5
0
5
EN ISO 10304, IC-method

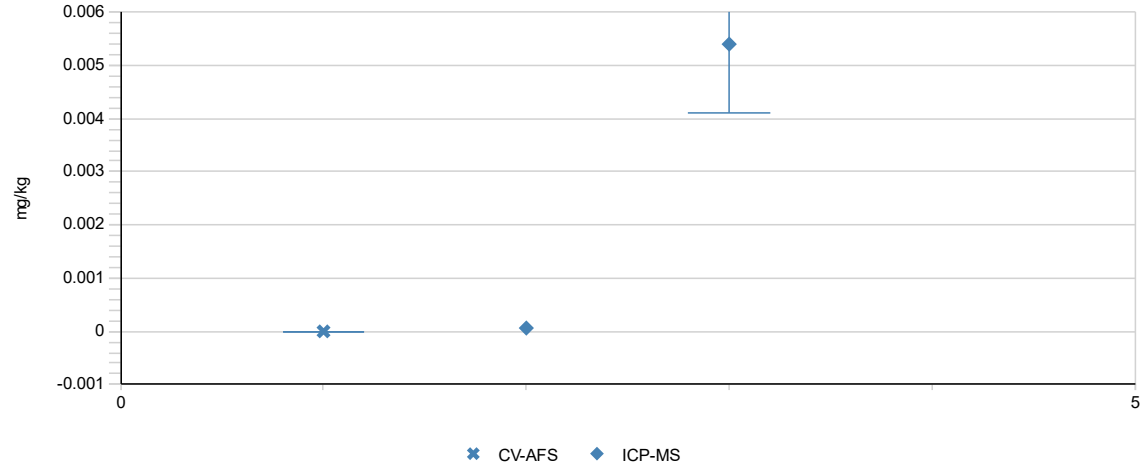
Measurand F Sample LS10upper

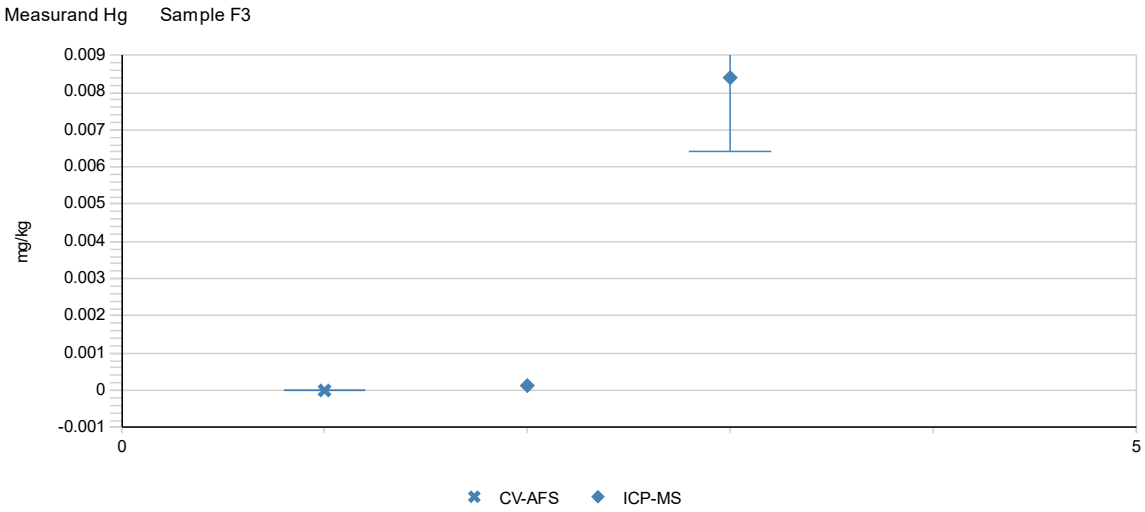


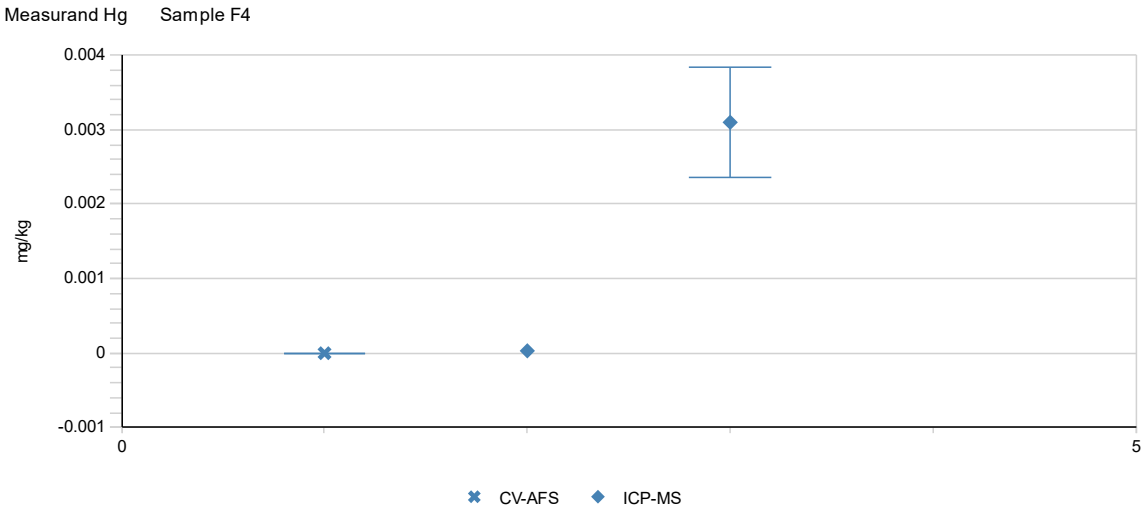

Measurand Hg Sample F1

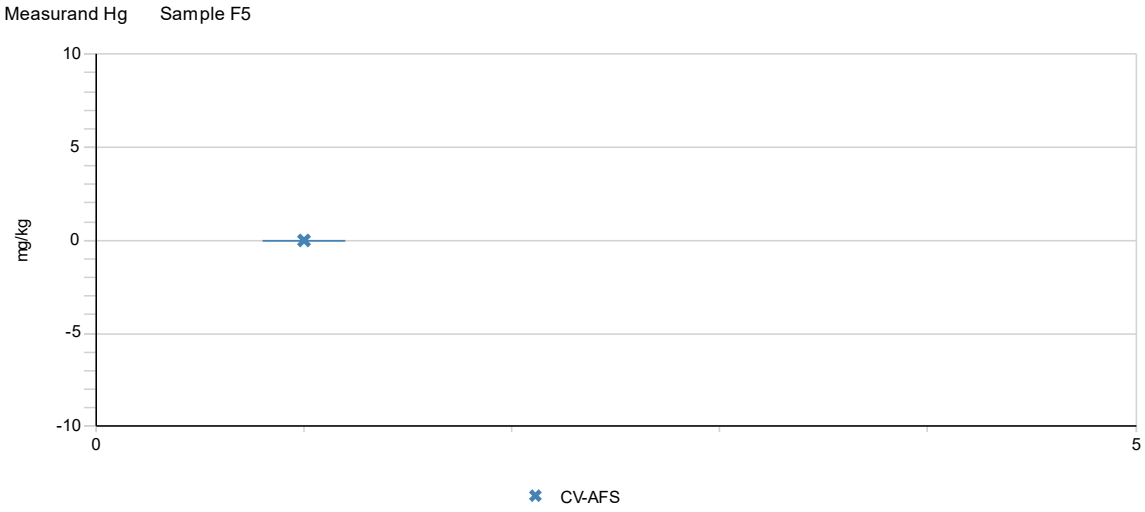



Measurand Hg Sample F2

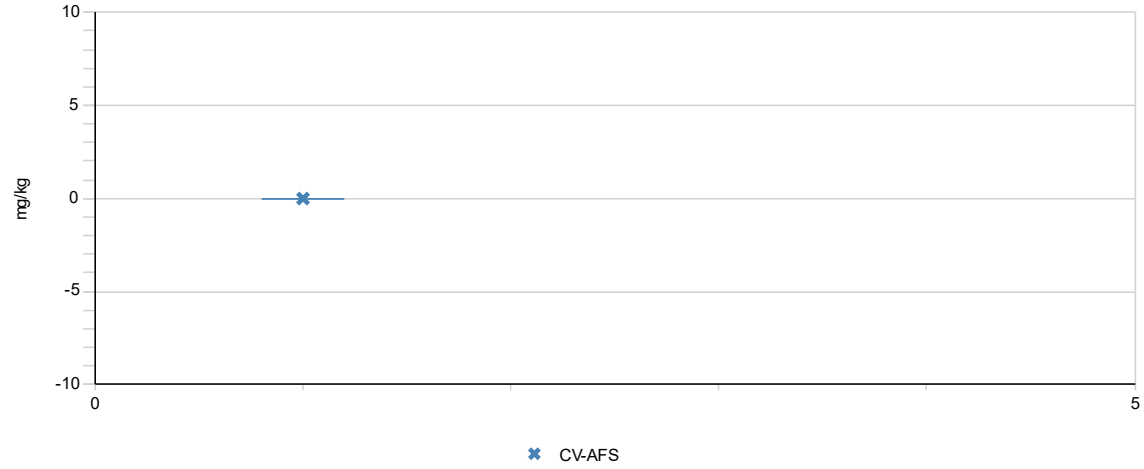



Measurand Hg Sample F3
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-0.001
mg/kg
0
5
CV-AFS
ICP-MS

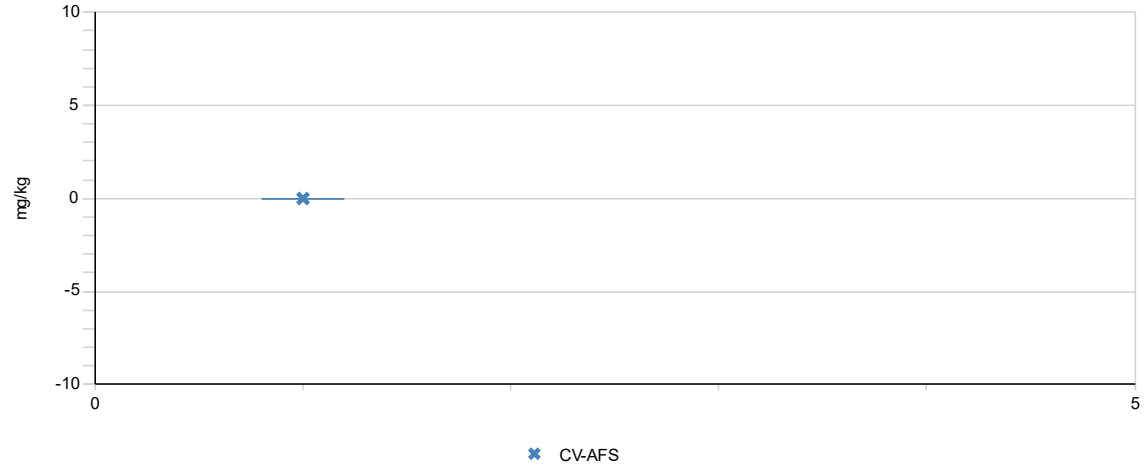

Measurand Hg Sample F4
0.004
0.003
0.002
0.001
0
-0.001
mg/kg
0
5
CV-AFS
ICP-MS


Measurand Hg Sample F5
10
5
0
-5
-10
mg/kg
0
5
CV-AFS

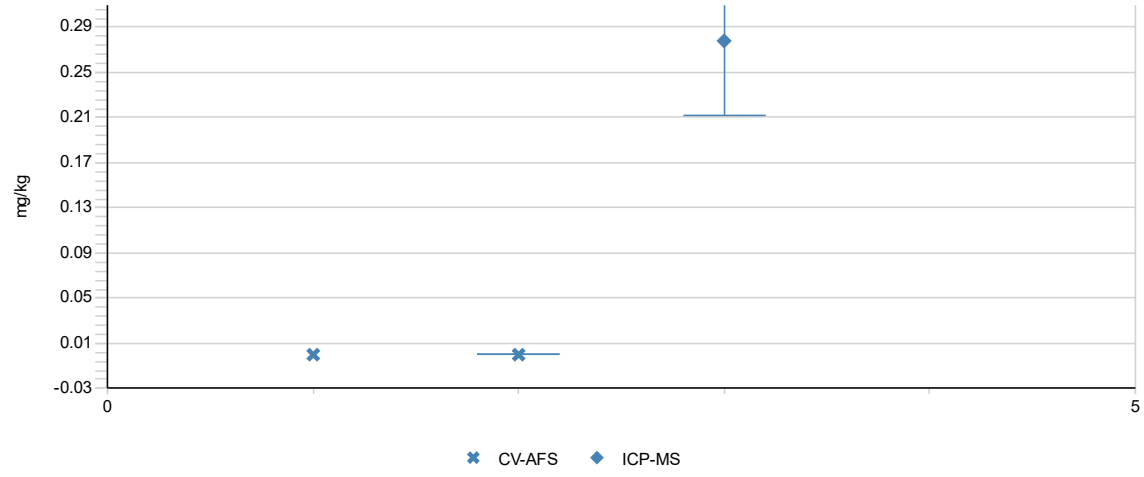
Measurand Hg Sample F6

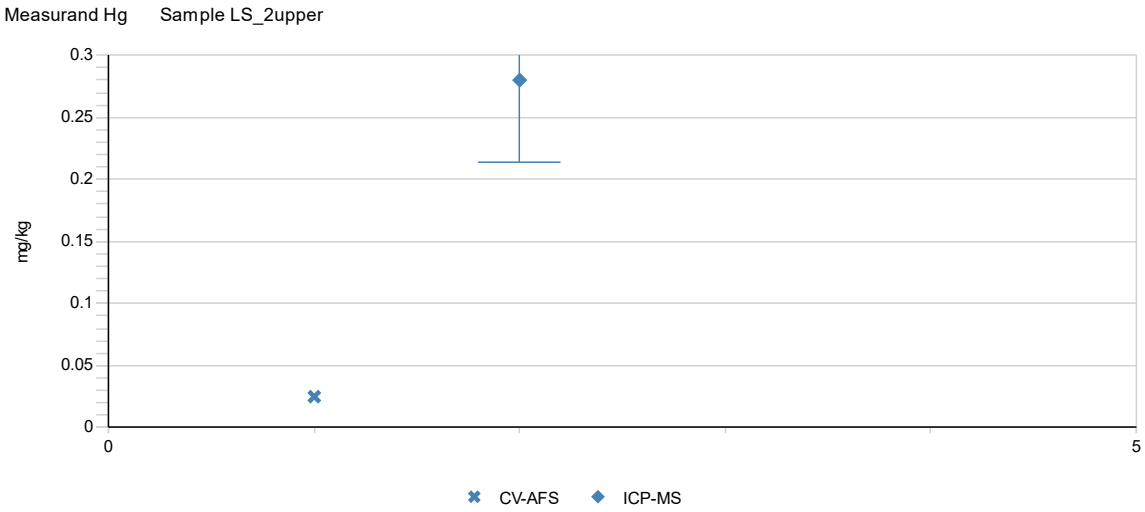


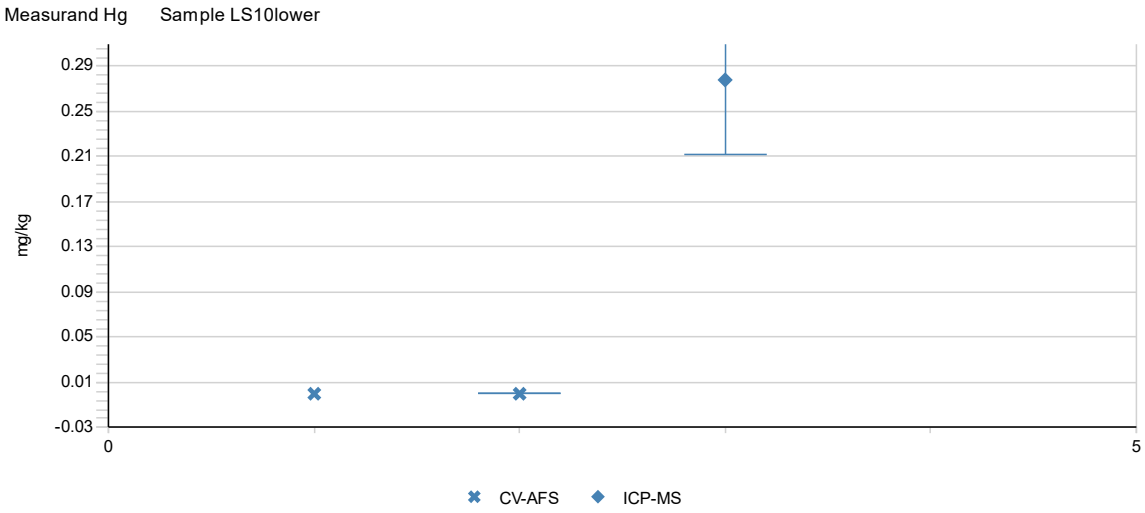

Measurand Hg Sample F7

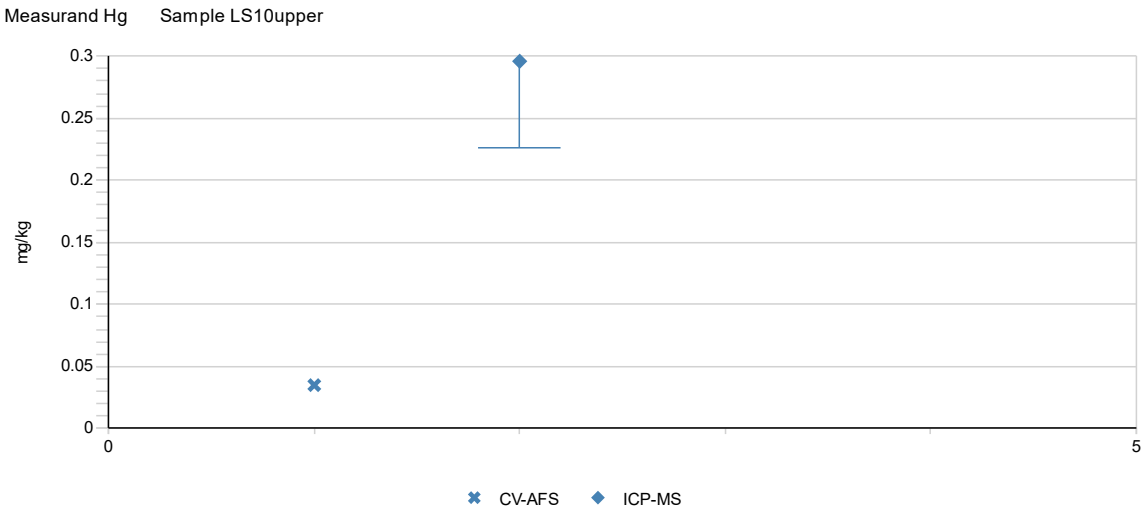



Measurand Hg Sample LS_2lower

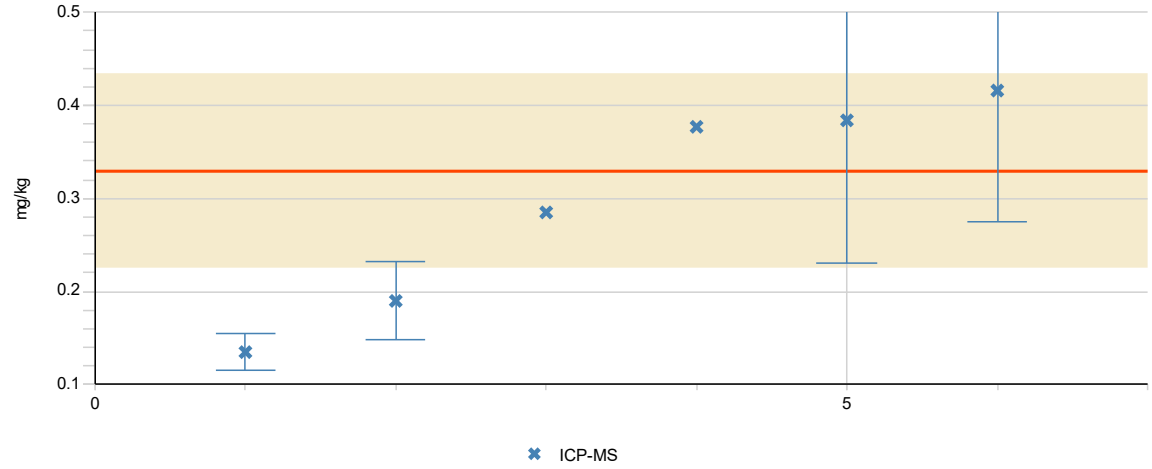



Measurand Hg
Sample LS_2upper
0.3
0.25
0.2
0.15
0.1
0.05
0
mg/kg
0
5
CV-AFS
ICP-MS

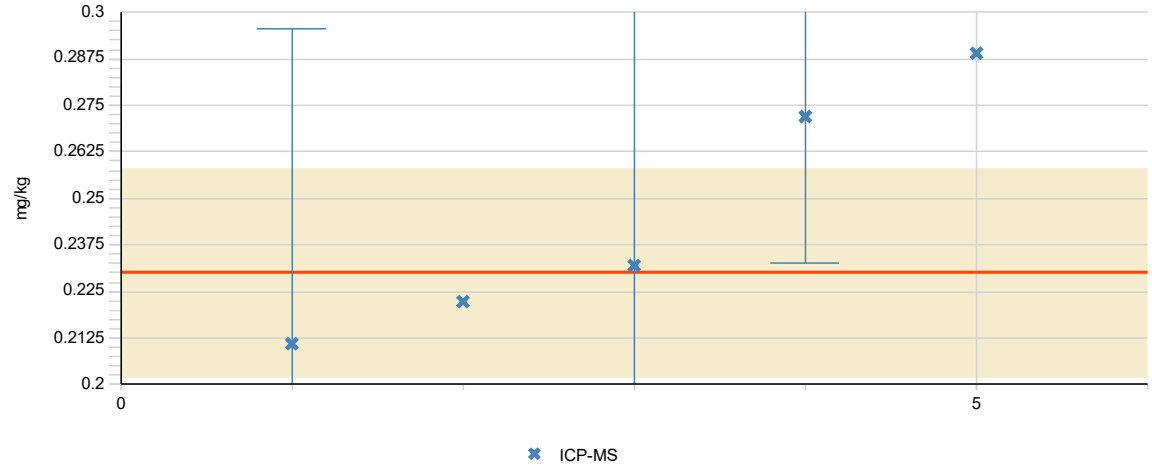

Measurand Hg
Sample LS10lower
0.29
0.25
0.21
0.17
0.13
0.09
0.05
0.01
-0.03
mg/kg
0
5
CV-AFS
ICP-MS


Measurand Hg
Sample LS10upper
0.3
0.25
0.2
0.15
0.1
0.05
0
mg/kg
0
5
CV-AFS
ICP-MS

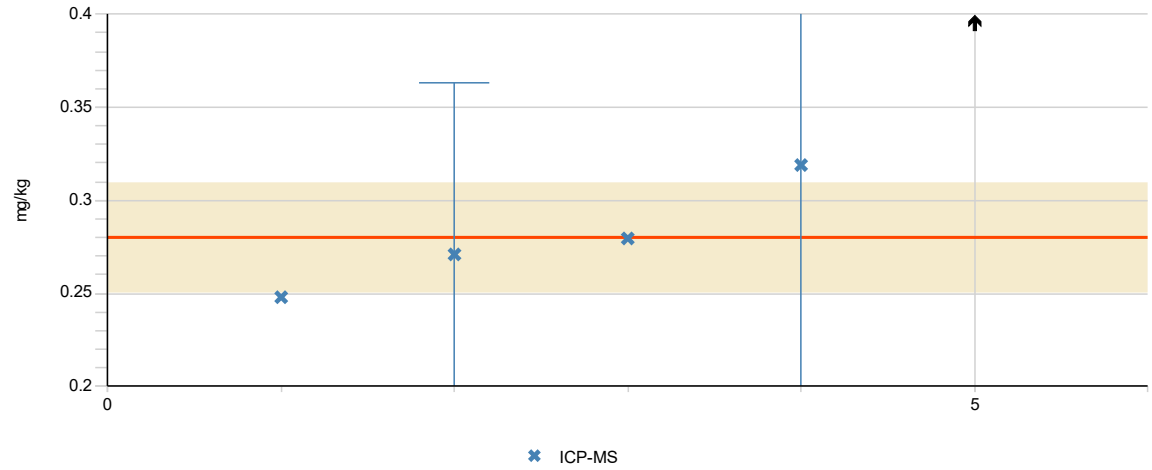
Measurand Mo Sample F1

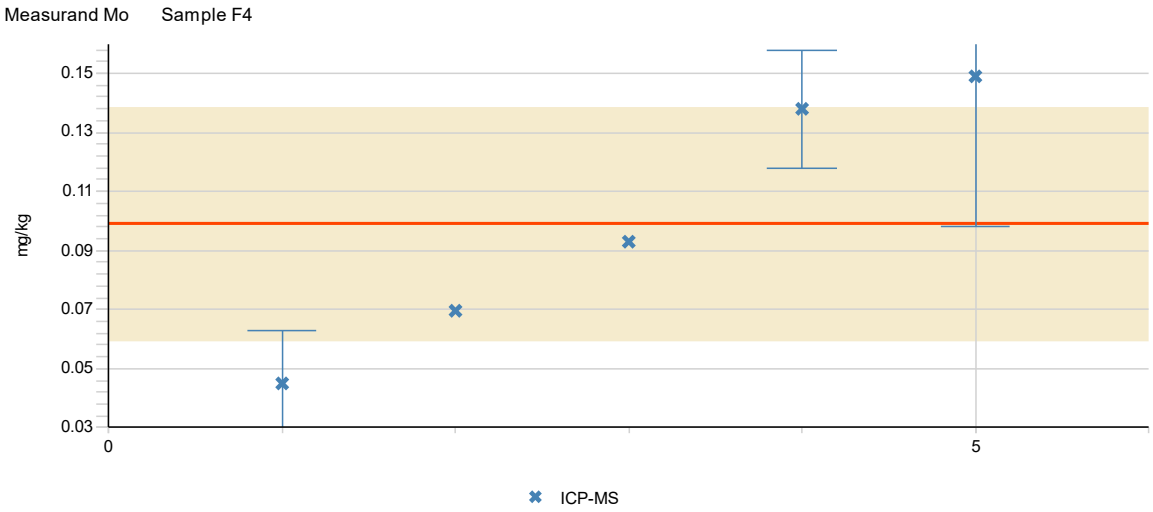


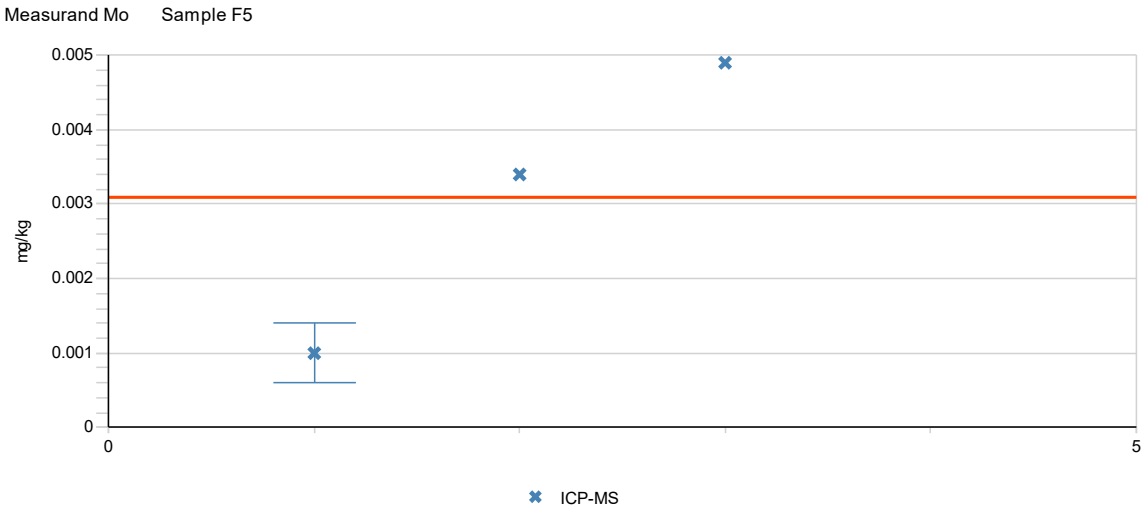

Measurand Mo Sample F2

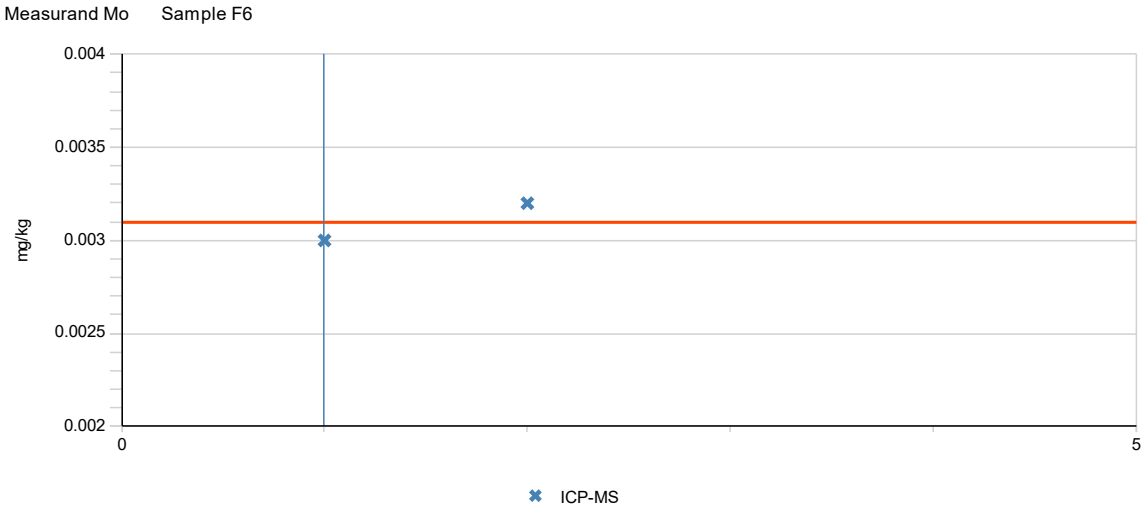



Measurand Mo Sample F3

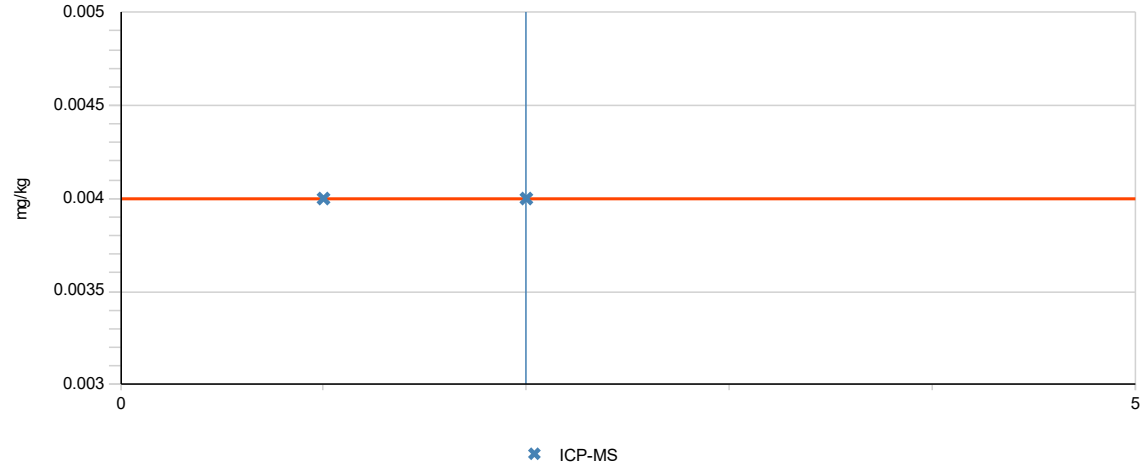



Measurand Mo
Sample F4
0.15
0.13
0.11
0.09
0.07
0.05
0.03
mg/kg
0
5
ICP-MS

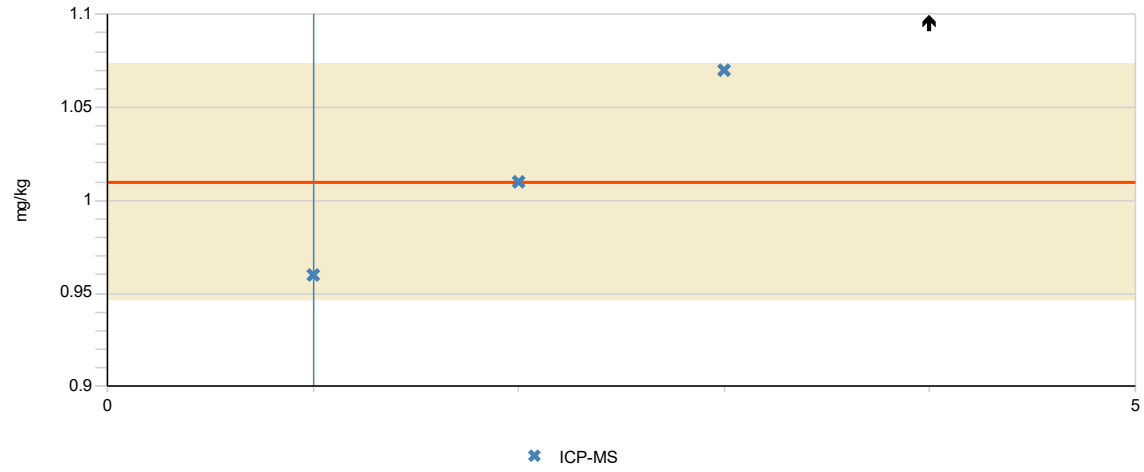

Measurand Mo
Sample F5
0.005
0.004
0.003
0.002
0.001
0
mg/kg
0
5
ICP-MS


Measurand Mo
Sample F6
0.004
0.0035
0.003
0.0025
0.002
mg/kg
0
5
ICP-MS

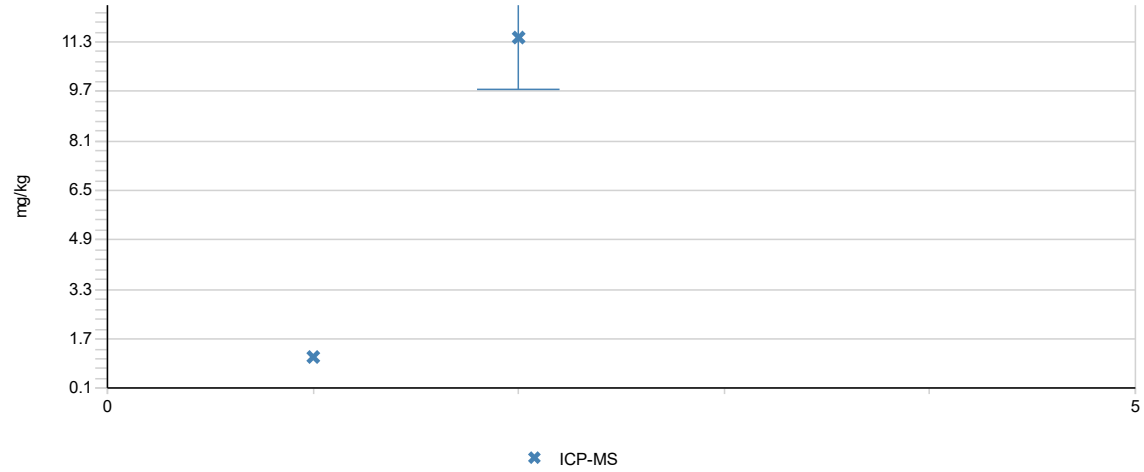
Measurand Mo Sample F7



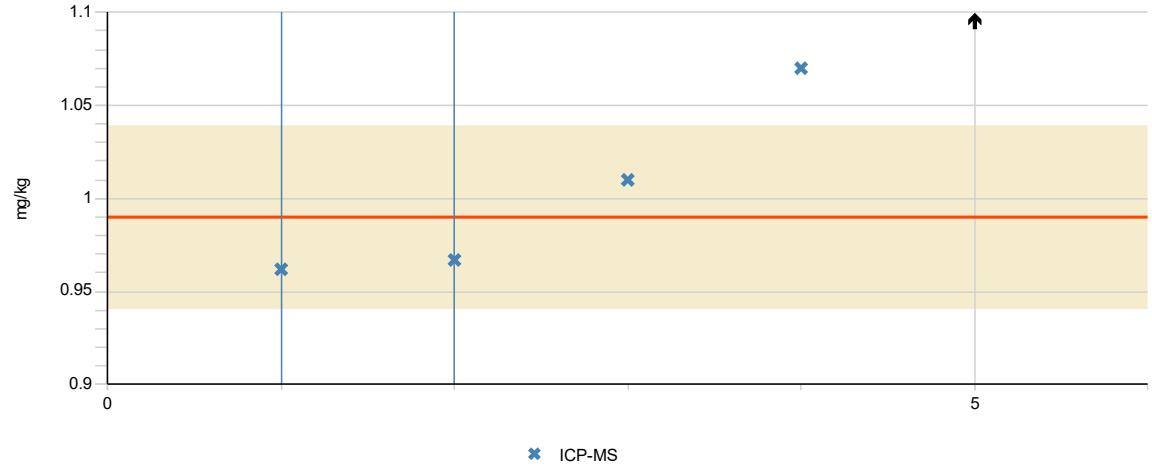

Measurand Mo Sample LS_2lower



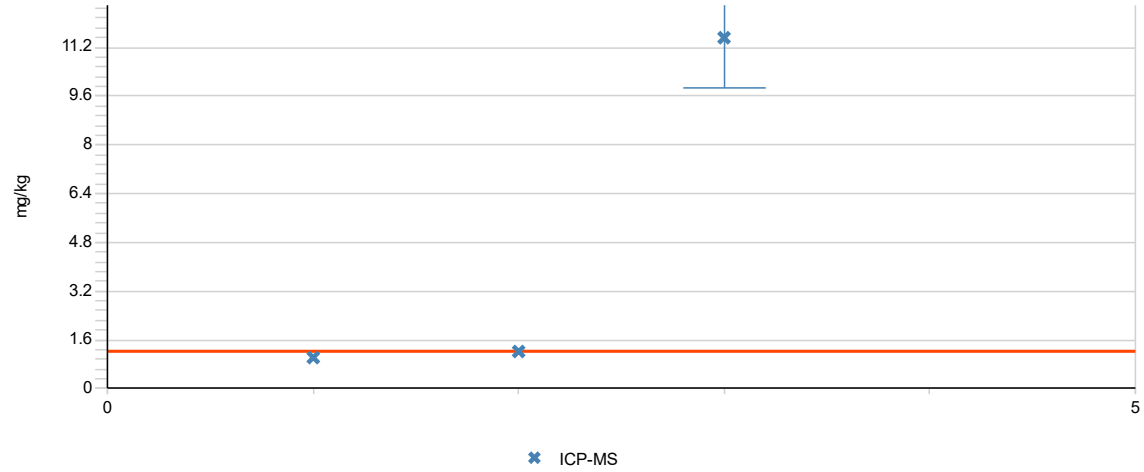

Measurand Mo Sample LS_2upper



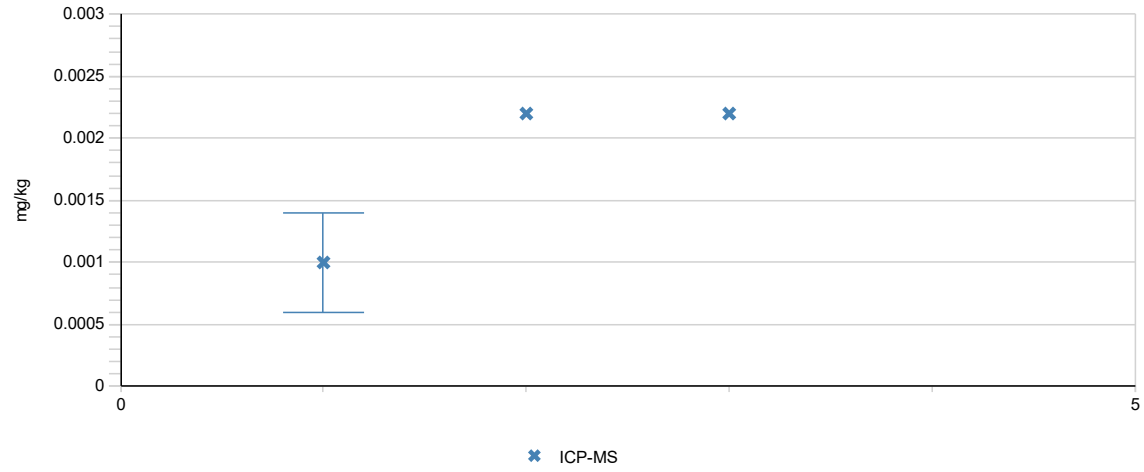
Measurand Mo Sample LS10lower

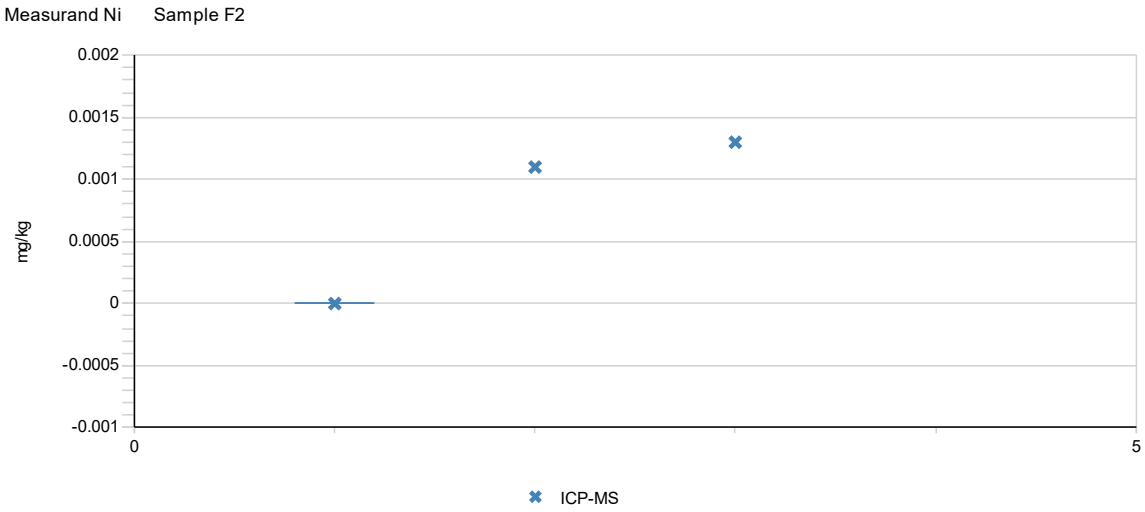


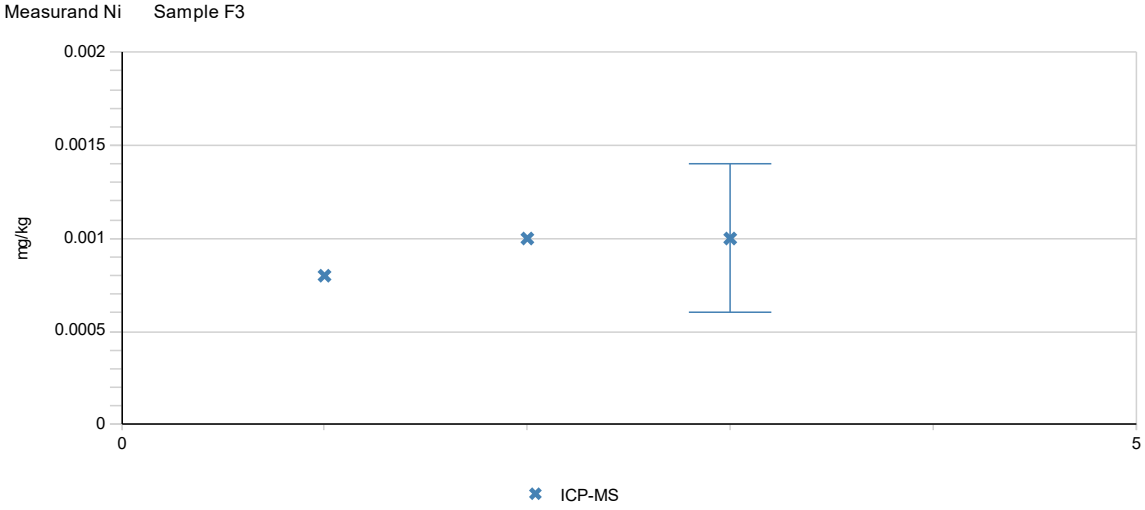

Measurand Mo Sample LS10upper

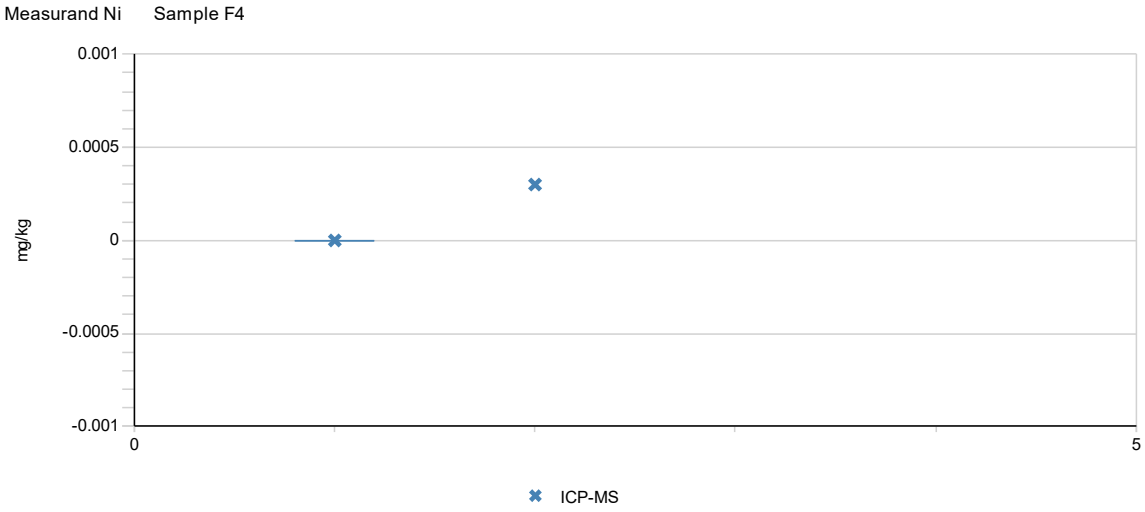


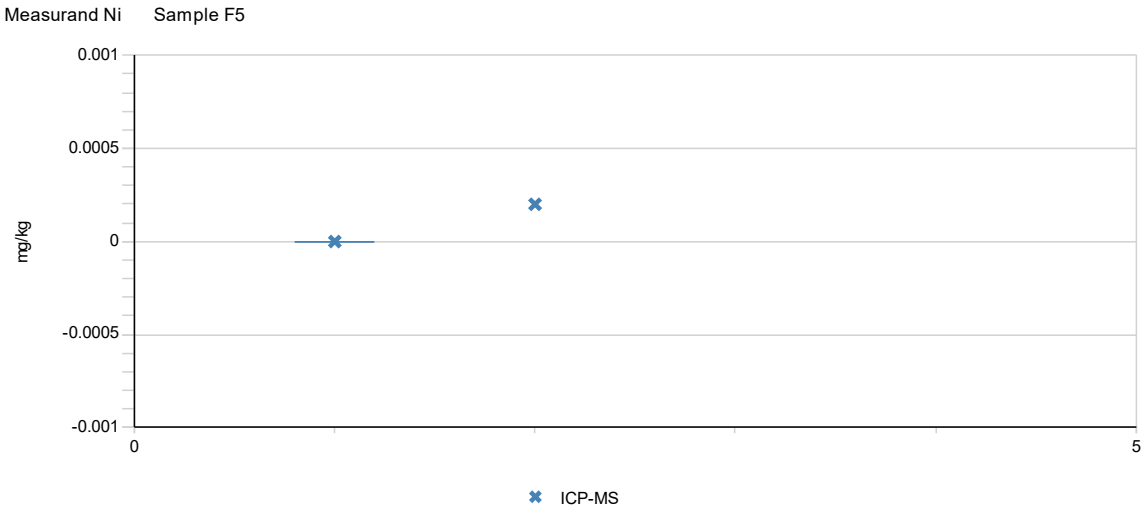

Measurand Ni Sample F1

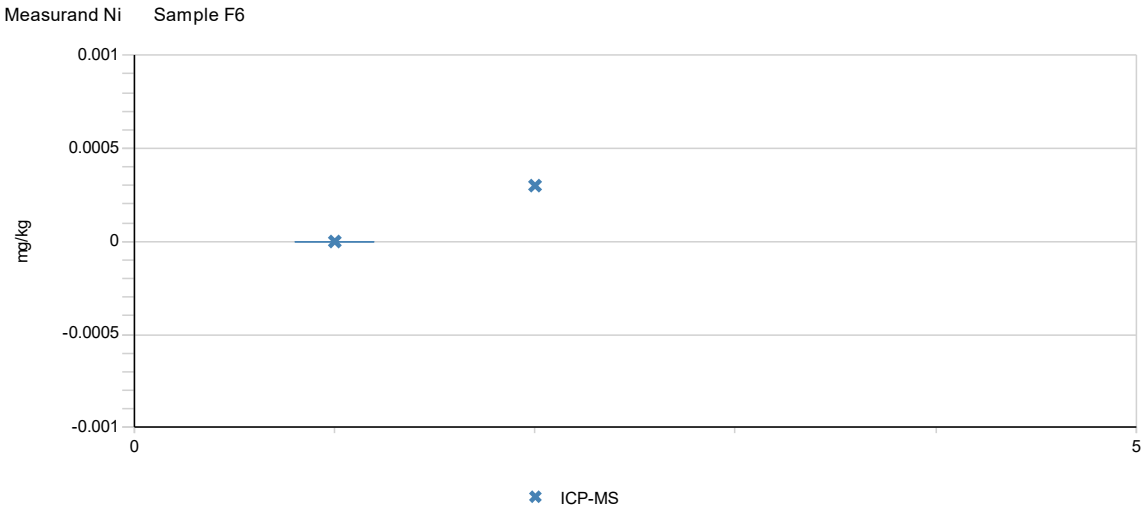


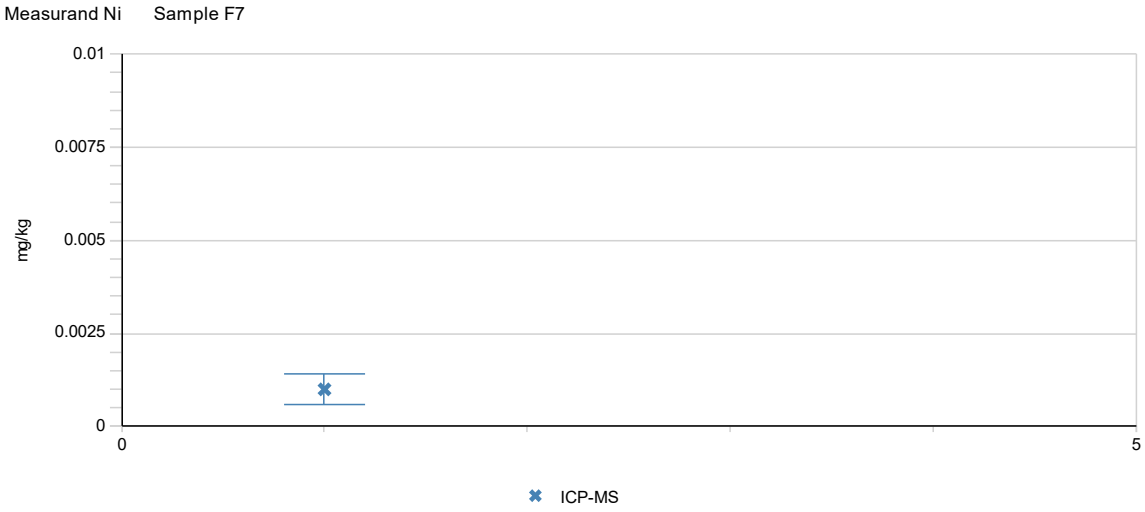

Measurand Ni Sample F2
0.002
0.0015
0.001
0.0005
0
-0.0005
-0.001
mg/kg
0
5
ICP-MS


Measurand Ni Sample F3
0.002
0.0015
0.001
0.0005
0
mg/kg
0
5
ICP-MS

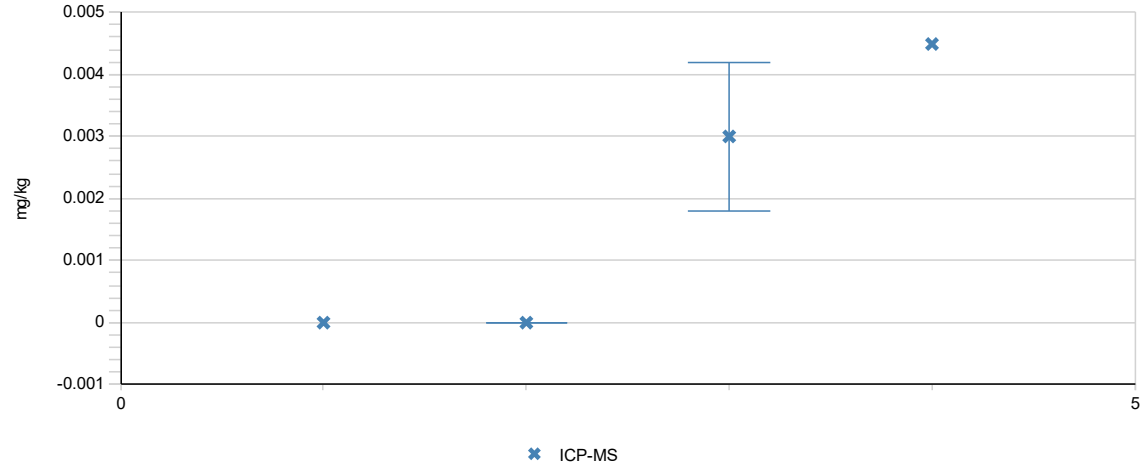

Measurand Ni Sample F4
0.001
0.0005
0
-0.0005
-0.001
mg/kg
0
5
ICP-MS


Measurand Ni Sample F5
0.001
0.0005
0
-0.0005
-0.001
mg/kg
0
5
ICP-MS

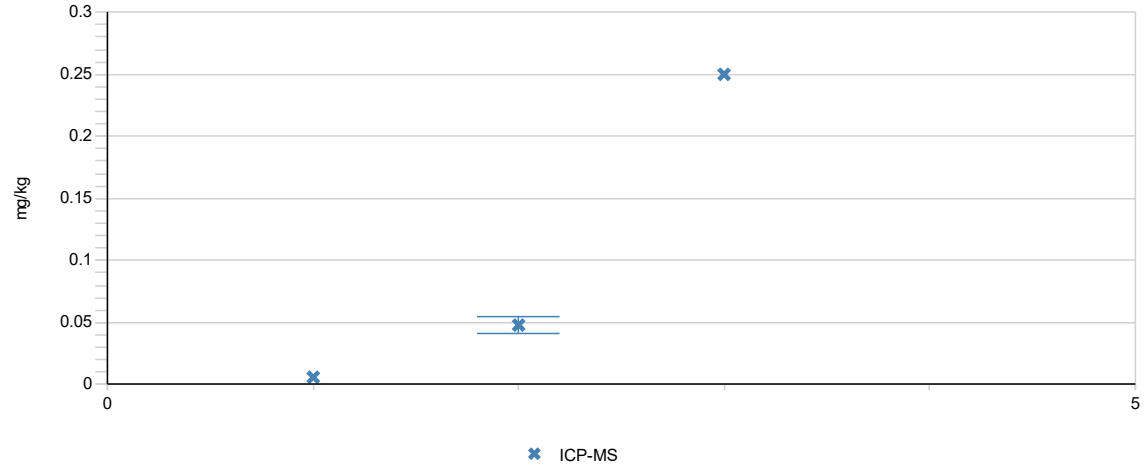

Measurand Ni Sample F6
0.001
0.0005
0
-0.0005
-0.001
mg/kg
0
5
ICP-MS


Measurand Ni Sample F7
0.01
0.0075
0.005
0.0025
0
mg/kg
0
5
ICP-MS

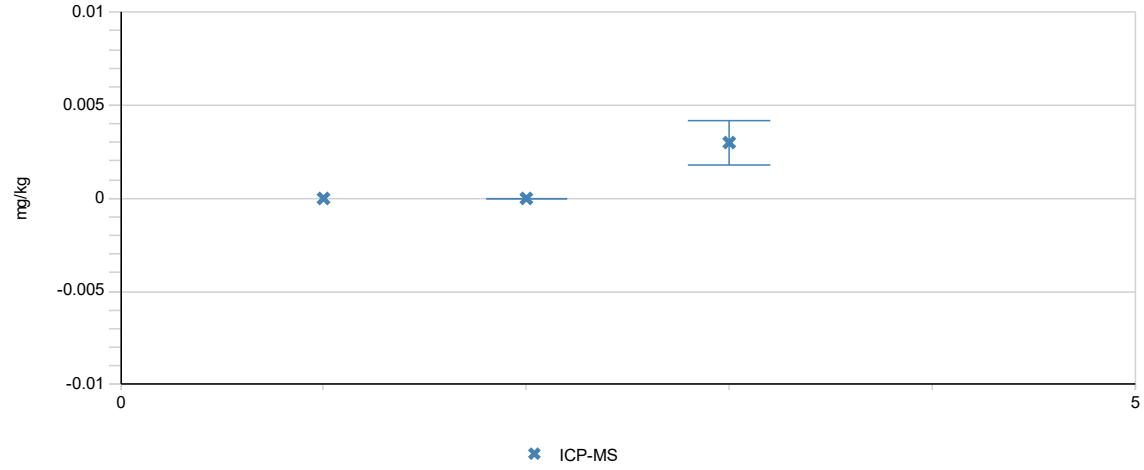
Measurand Ni Sample LS_2lower



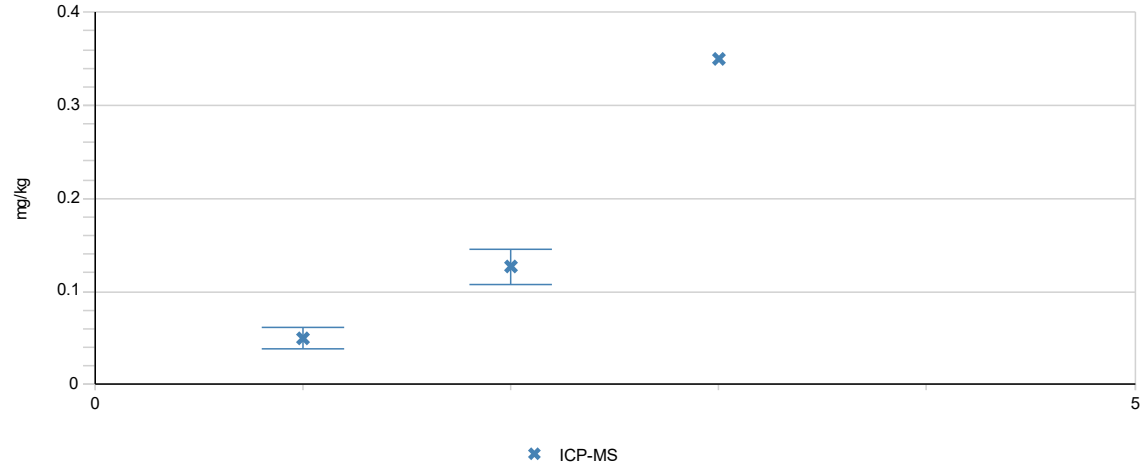

Measurand Ni Sample LS_2upper



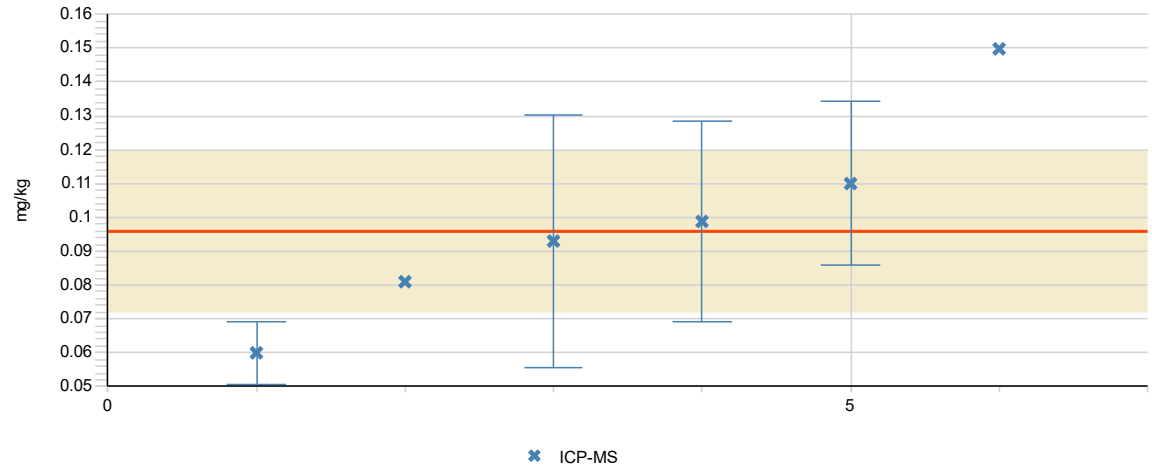

Measurand Ni Sample LS10lower



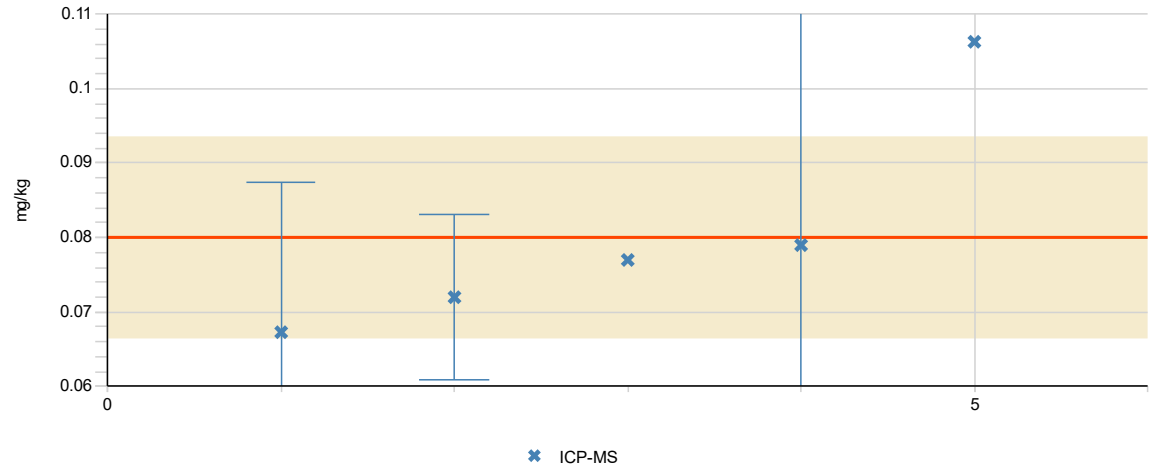
Measurand Ni Sample LS10upper



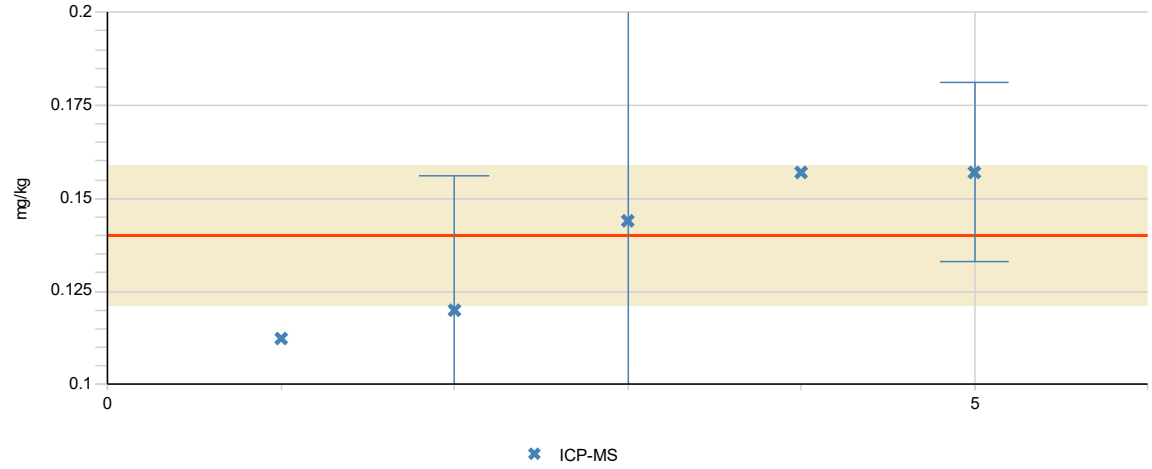

Measurand Pb Sample F1



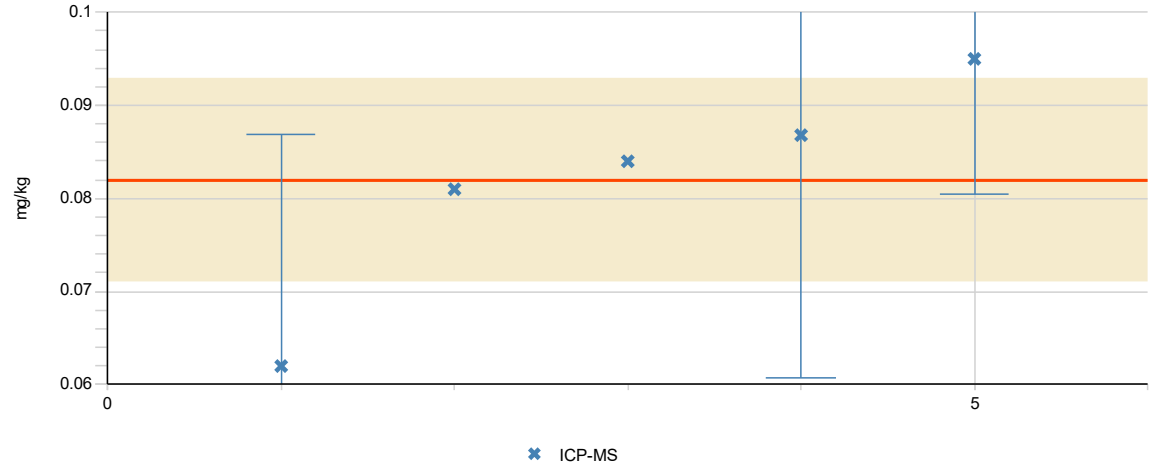

Measurand Pb Sample F2



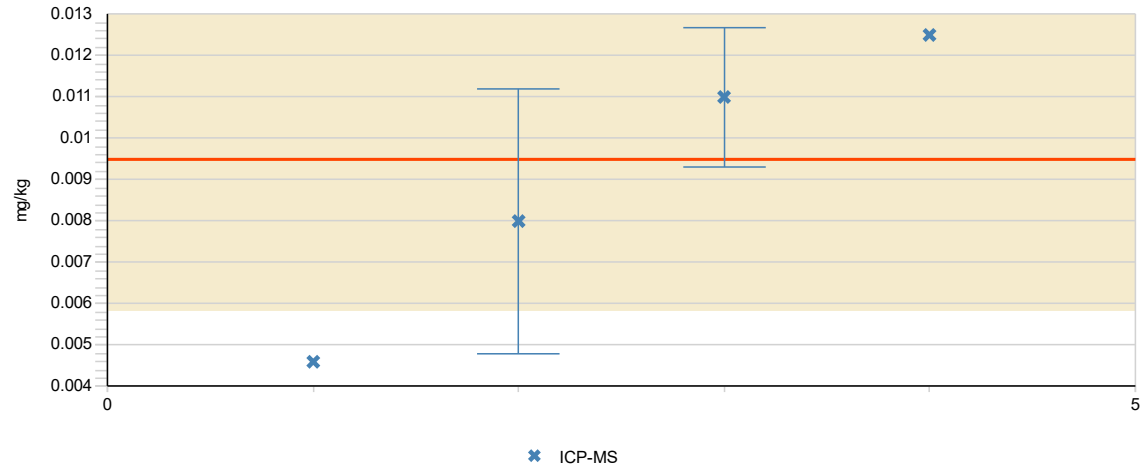
Measurand Pb Sample F3



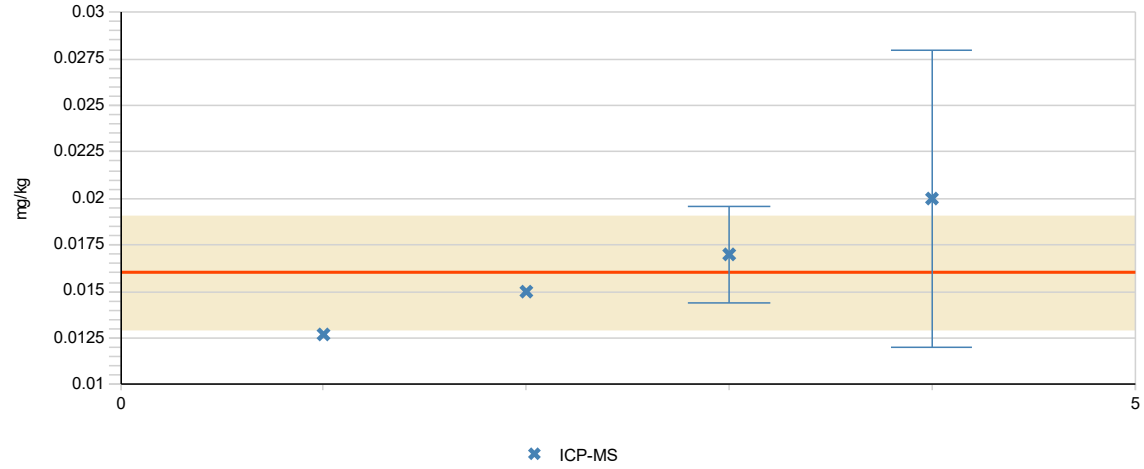

Measurand Pb Sample F4



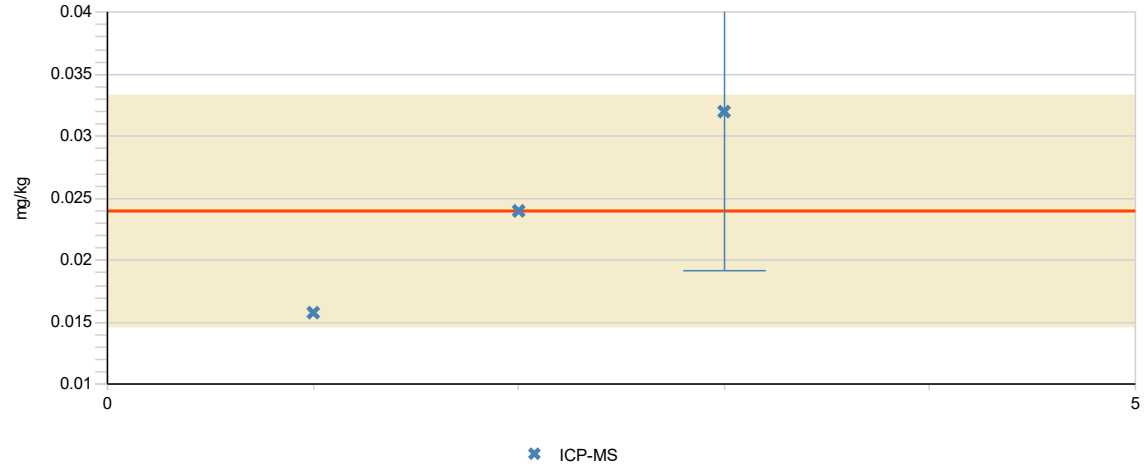

Measurand Pb Sample F5



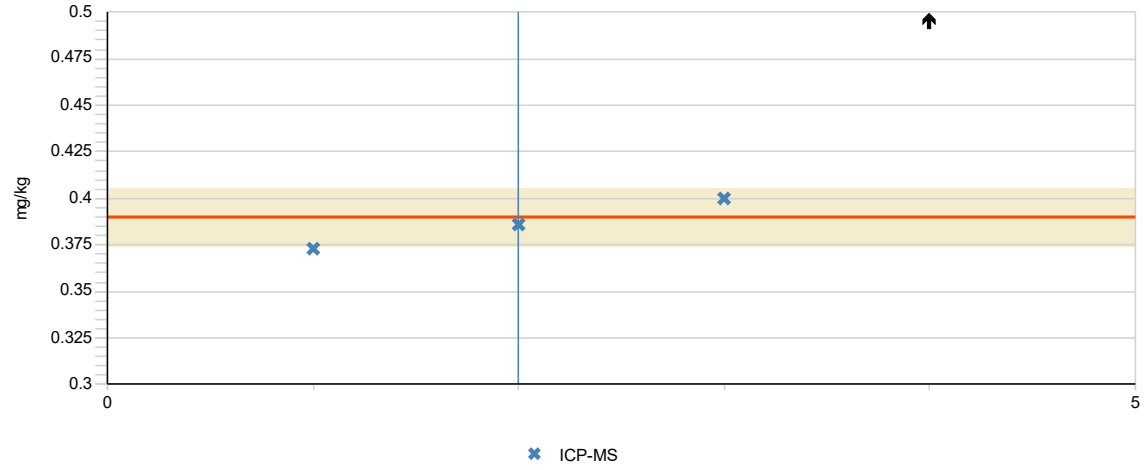
Measurand Pb Sample F6



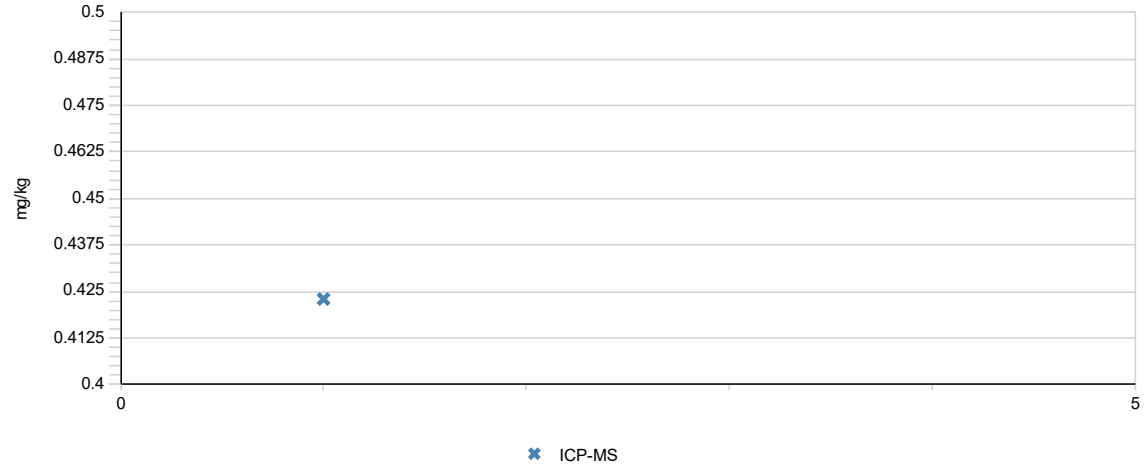

Measurand Pb Sample F7



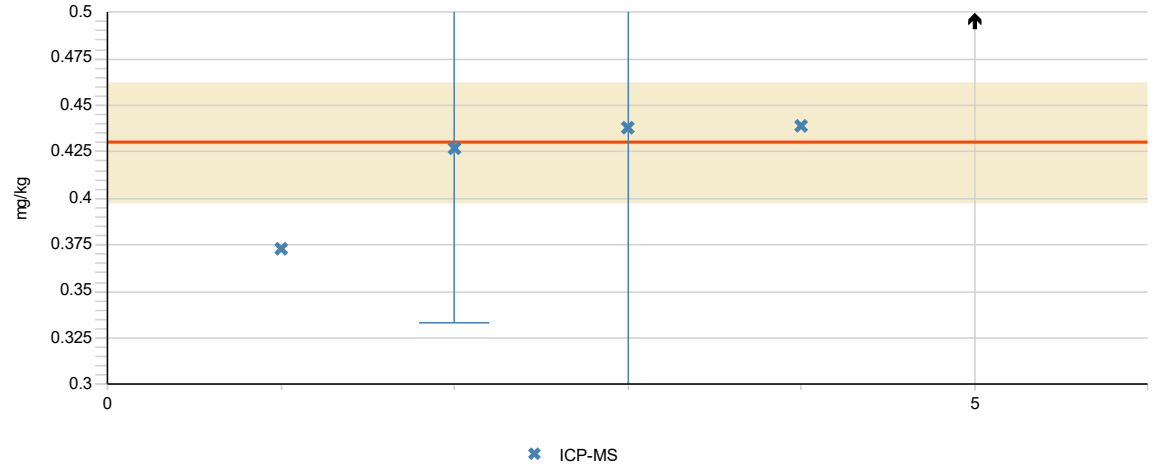

Measurand Pb Sample LS_2lower



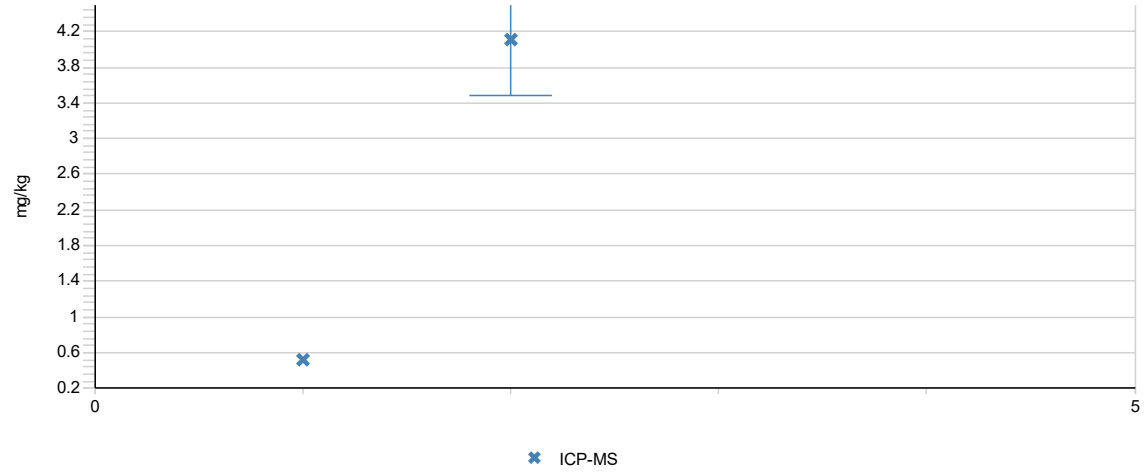
Measurand Pb Sample LS_2upper

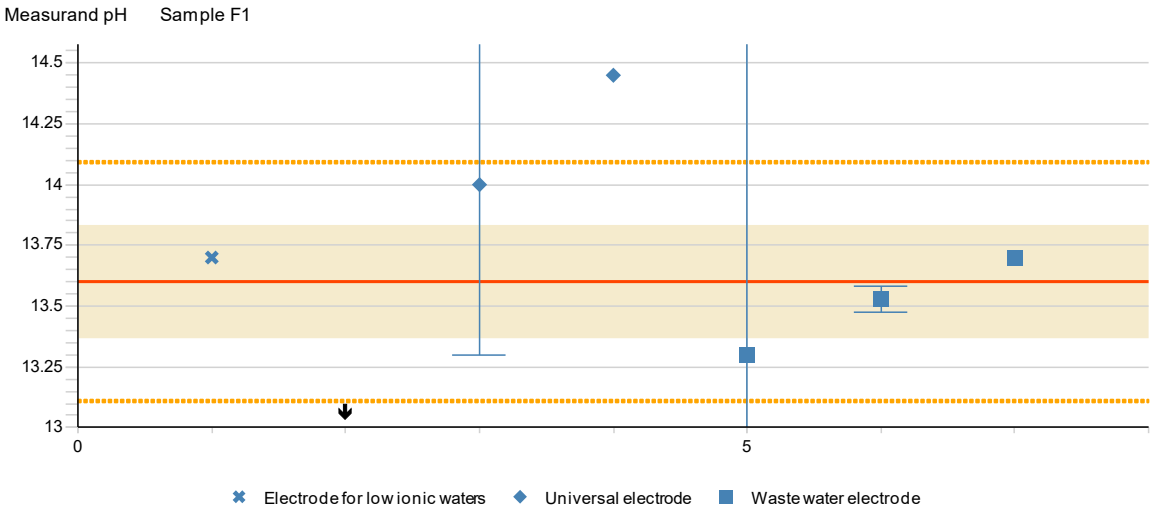


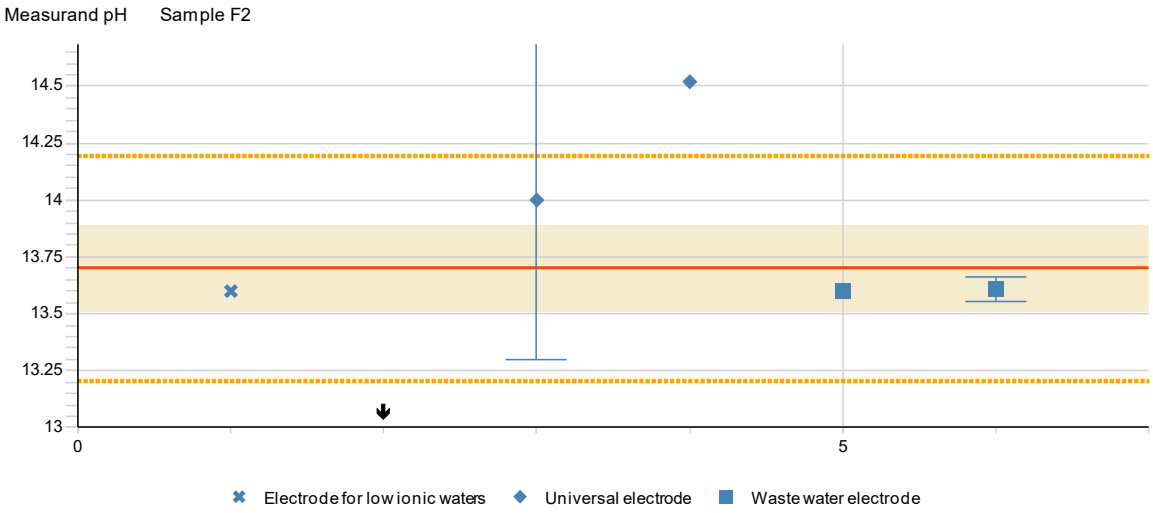

Measurand Pb Sample LS10lower

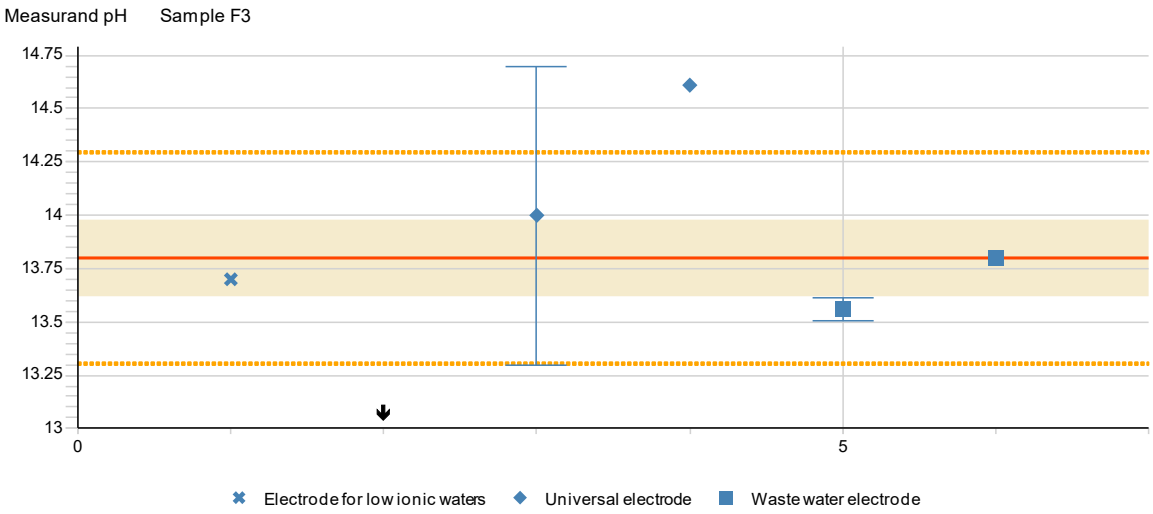



Measurand Pb Sample LS10upper

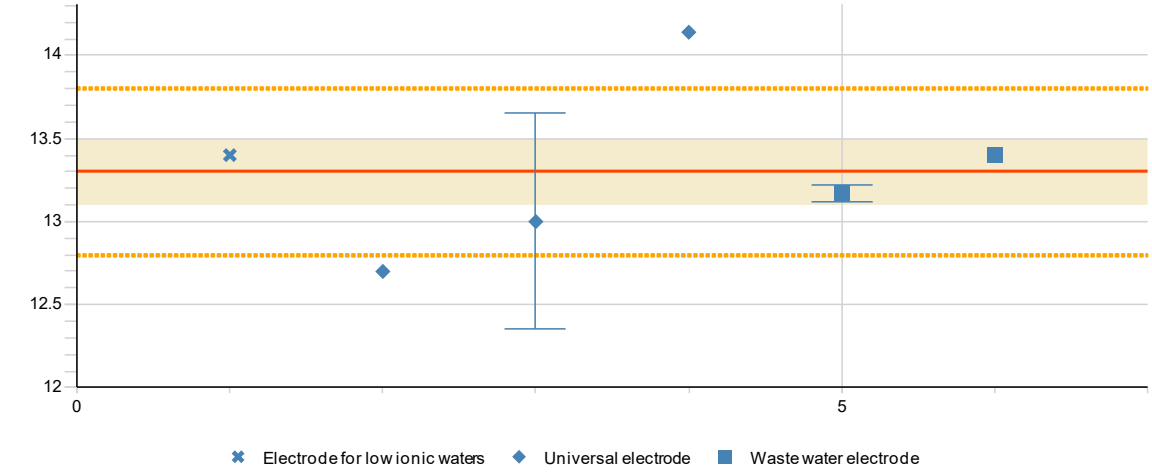



Measurand pH Sample F1
14.5
14.25
14
13.75
13.5
13.25
13
0
5
Electrode for low ionic waters
Universal electrode
Waste water electrode

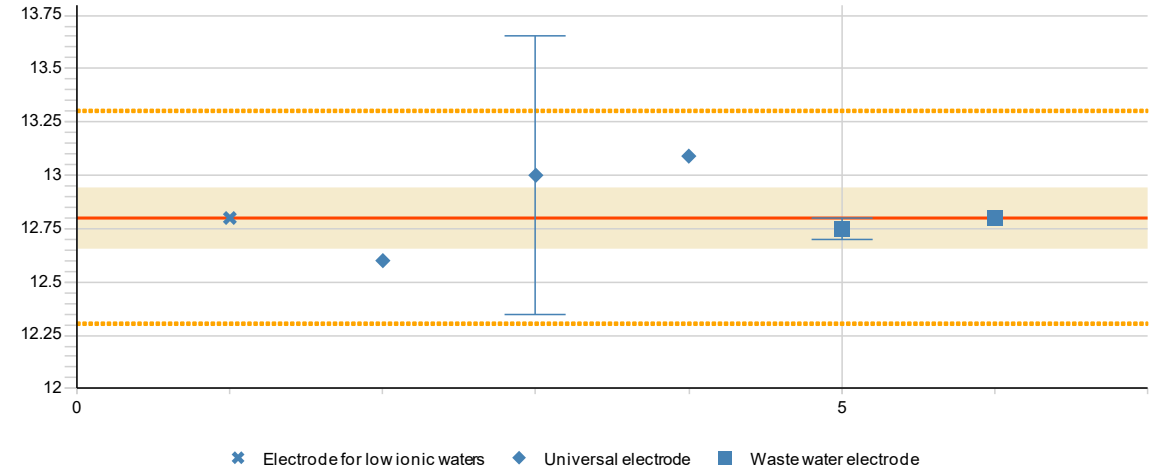

Measurand pH Sample F2
14.5
14.25
14
13.75
13.5
13.25
13
0
5
Electrode for low ionic waters
Universal electrode
Waste water electrode


Measurand pH Sample F3
14.75
14.5
14.25
14
13.75
13.5
13.25
13
0
5
Electrode for low ionic waters
Universal electrode
Waste water electrode

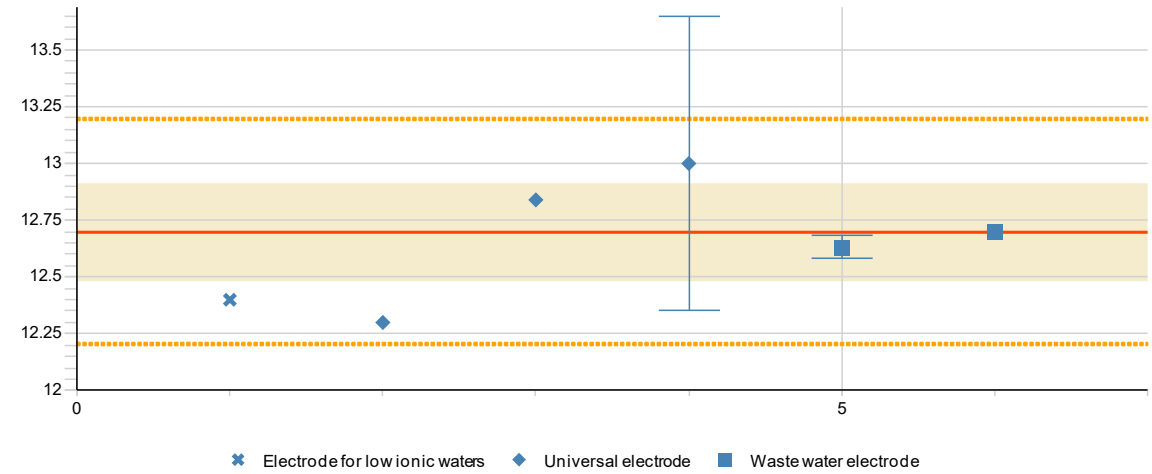
Measurand pH Sample F4



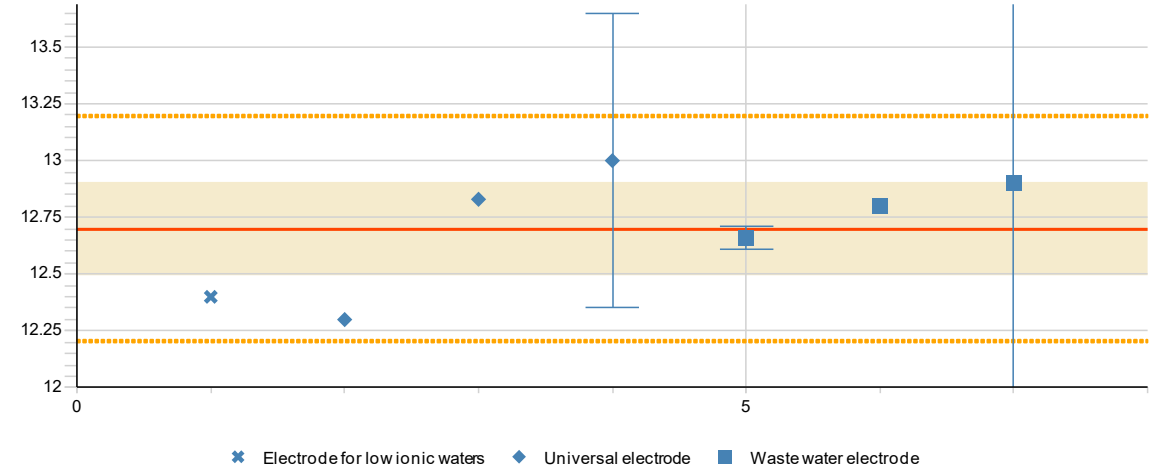

Measurand pH Sample F5



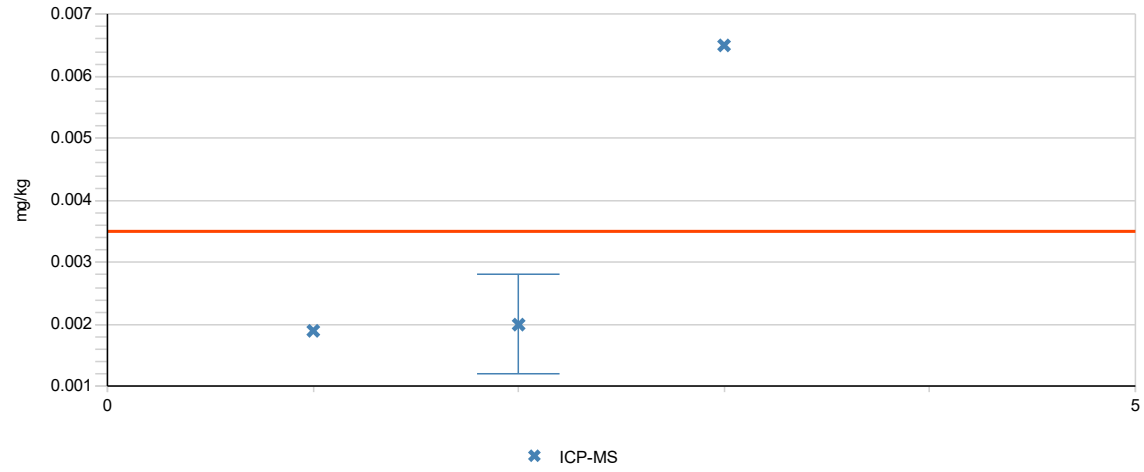

Measurand pH Sample F6



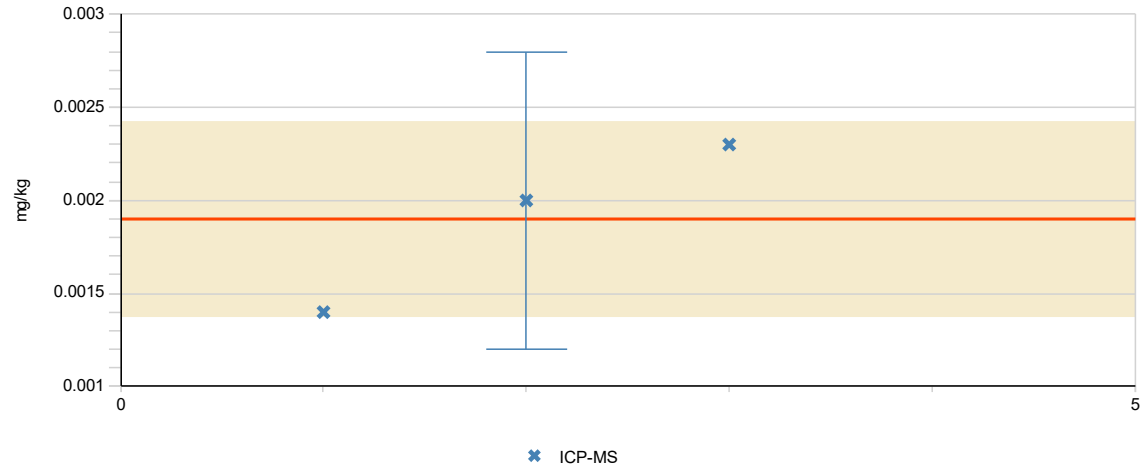
Measurand pH Sample F7



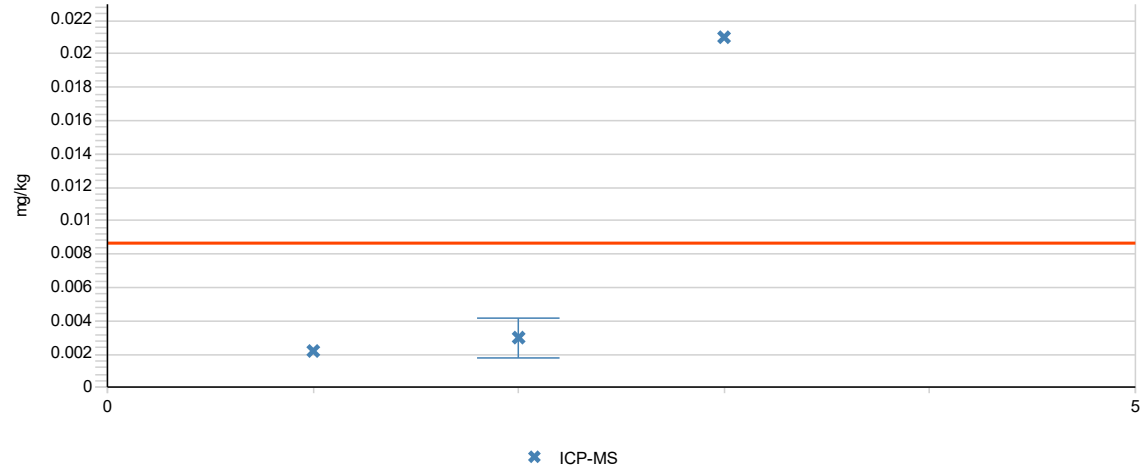

Measurand Sb Sample F1



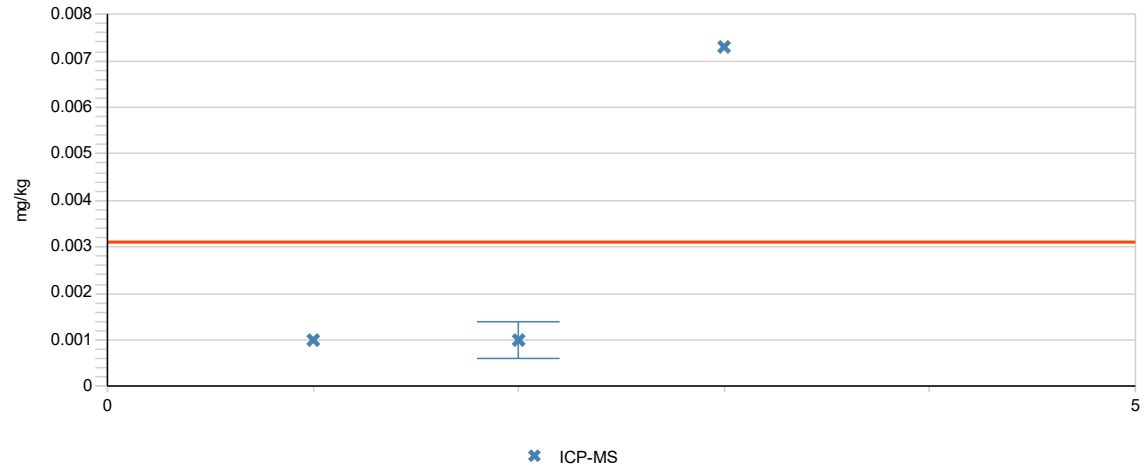

Measurand Sb Sample F2



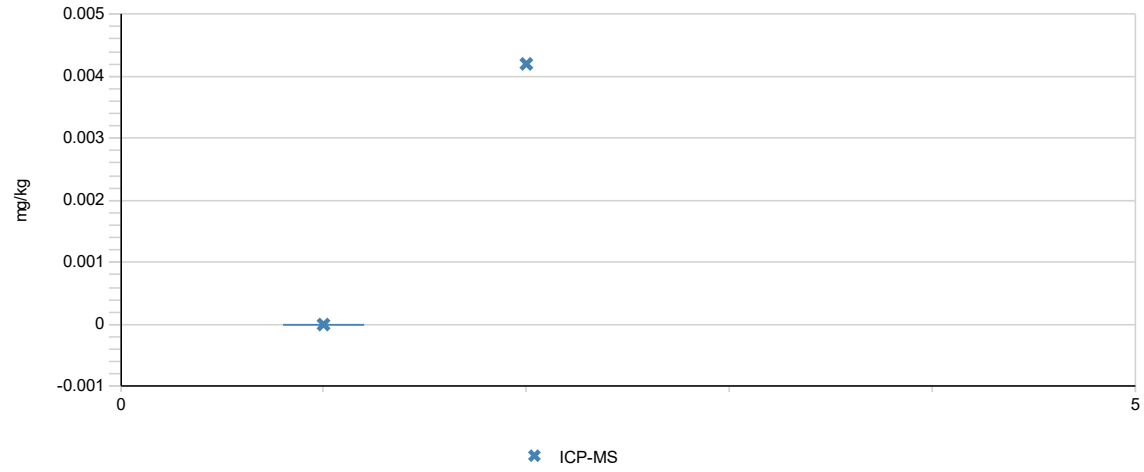
Measurand Sb Sample F3

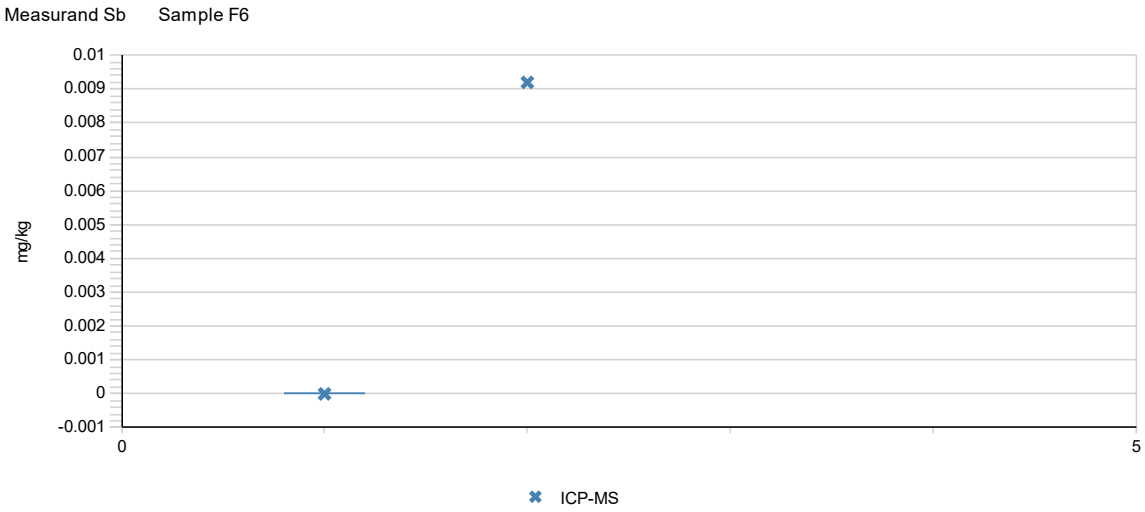


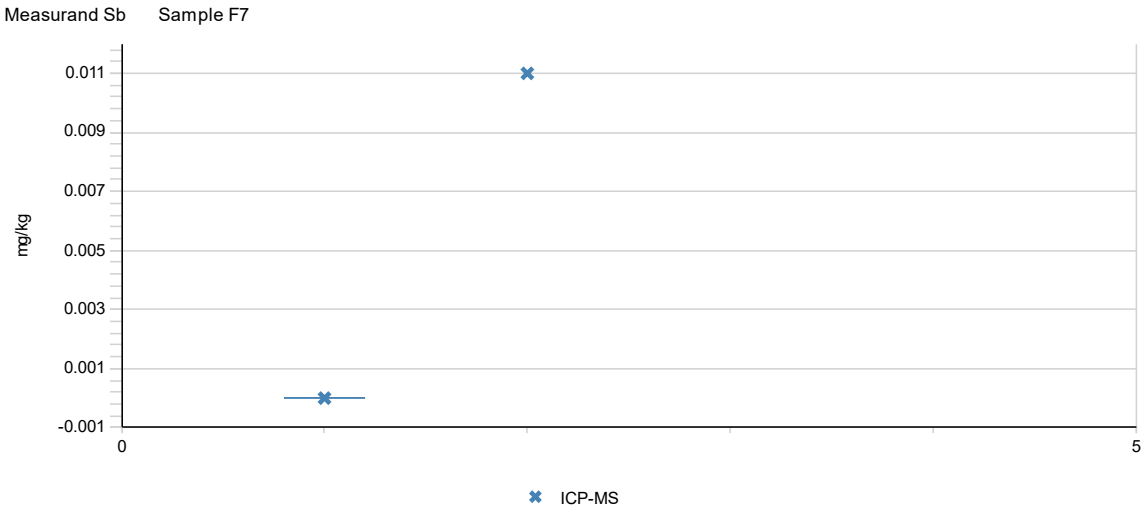

Measurand Sb Sample F4

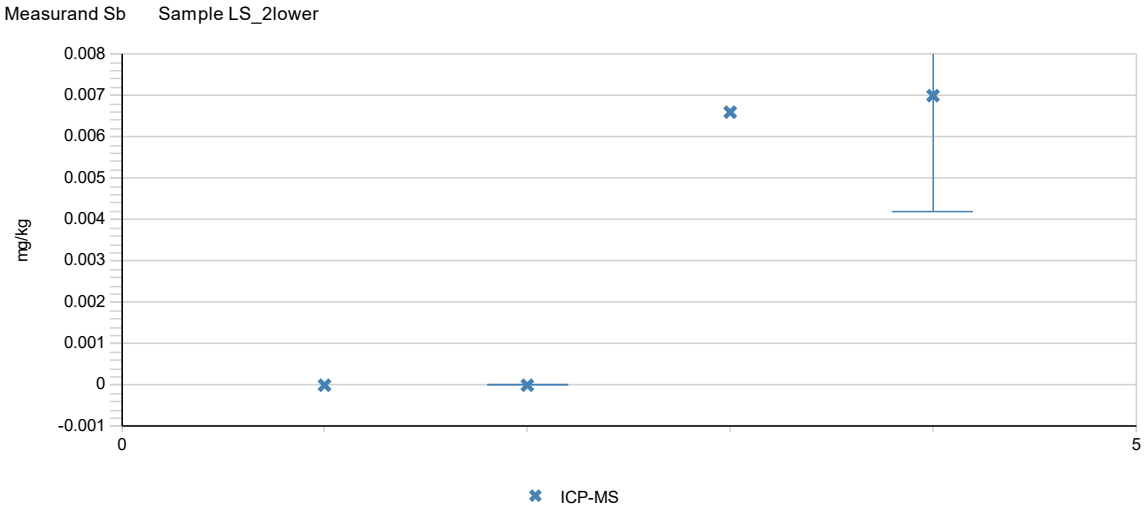


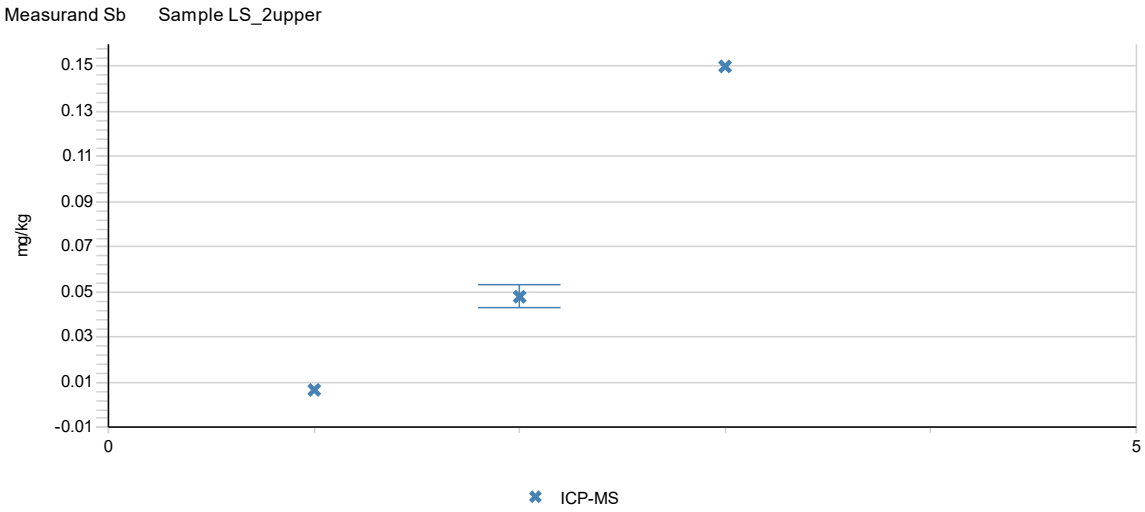

Measurand Sb Sample F5

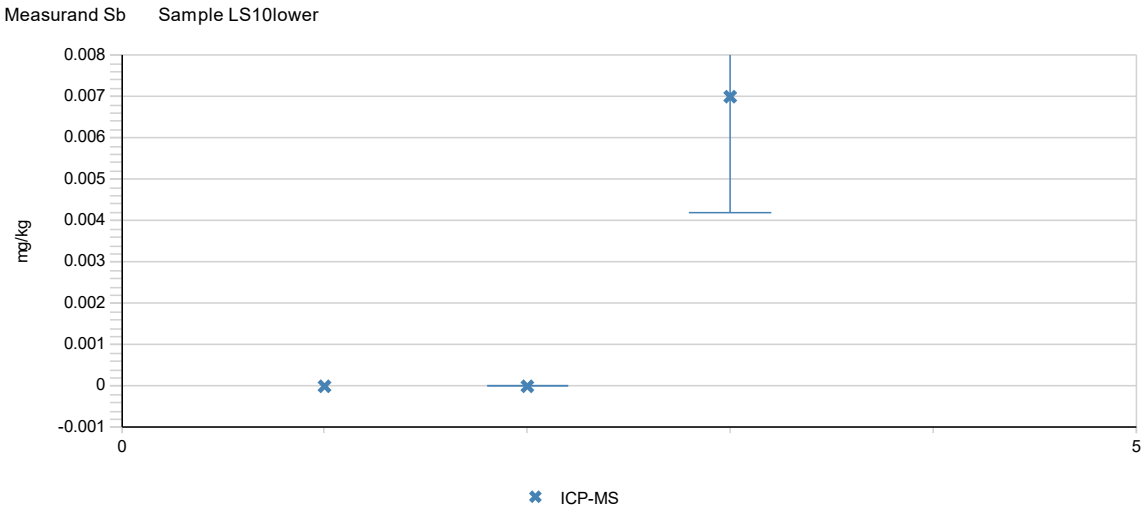


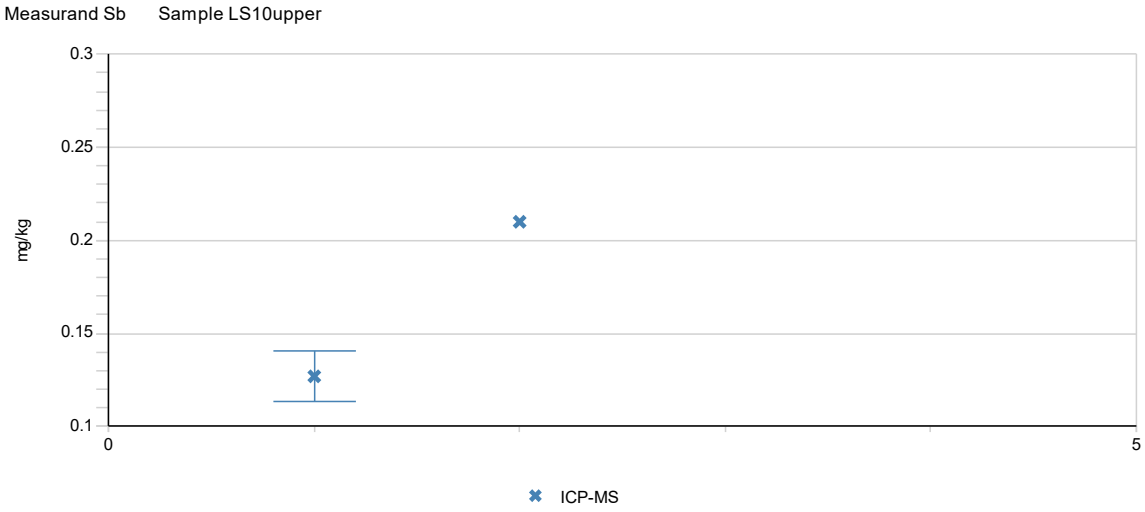

Measurand Sb
Sample F6
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-0.001
mg/kg
0
5
ICP-MS

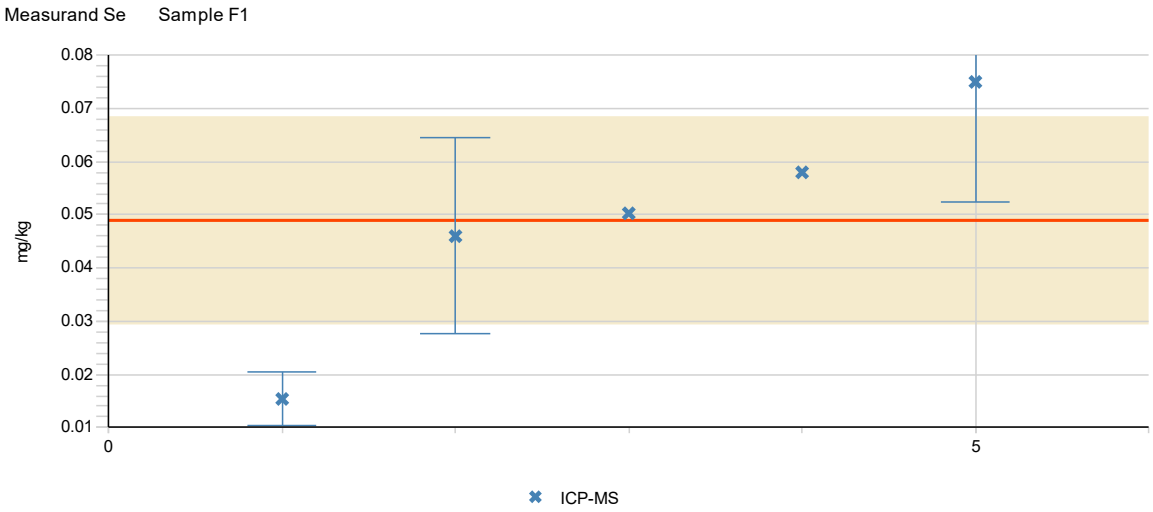

Measurand Sb
Sample F7
0.011
0.009
0.007
0.005
0.003
0.001
-0.001
mg/kg
0
5
ICP-MS

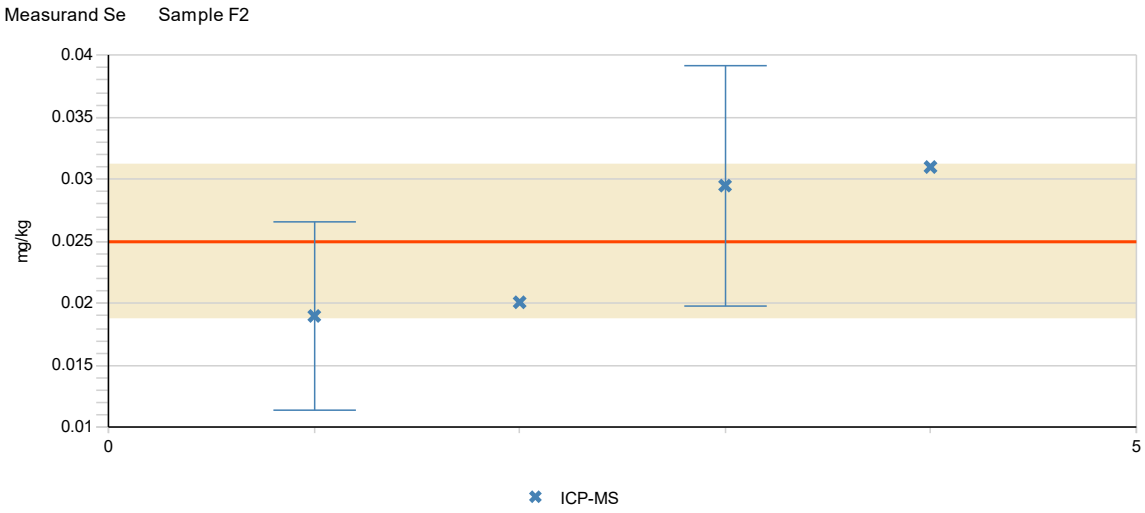

Measurand Sb
Sample LS_2lower
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-0.001
mg/kg
0
5
ICP-MS

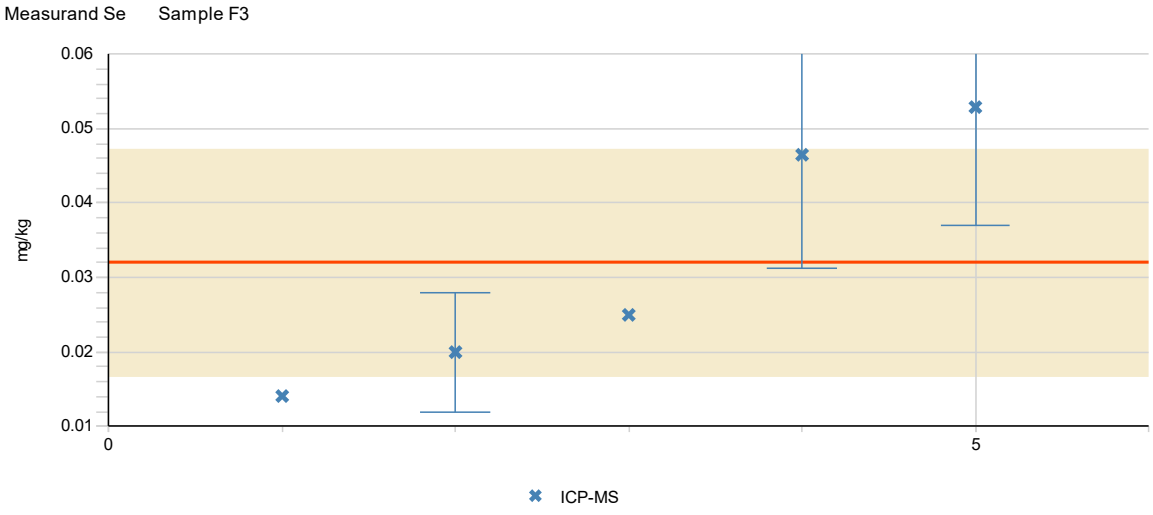

Measurand Sb
Sample LS_2upper
0.15
0.13
0.11
0.09
0.07
0.05
0.03
0.01
-0.01
mg/kg
0
5
ICP-MS

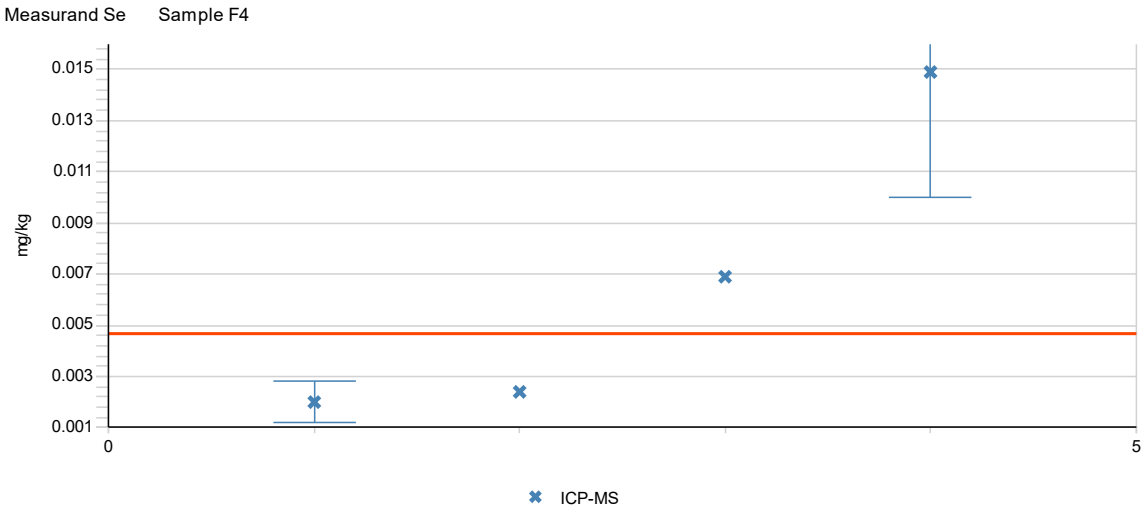

Measurand Sb
Sample LS10lower
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
-0.001
mg/kg
0
5
ICP-MS

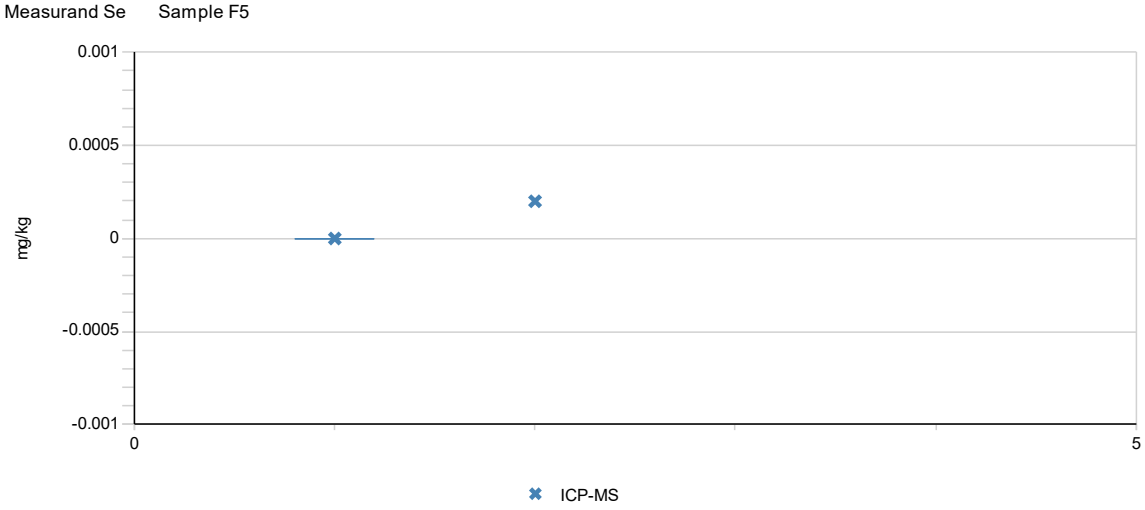

Measurand Sb
Sample LS10upper
0.3
0.25
0.2
0.15
0.1
mg/kg
0
5
ICP-MS

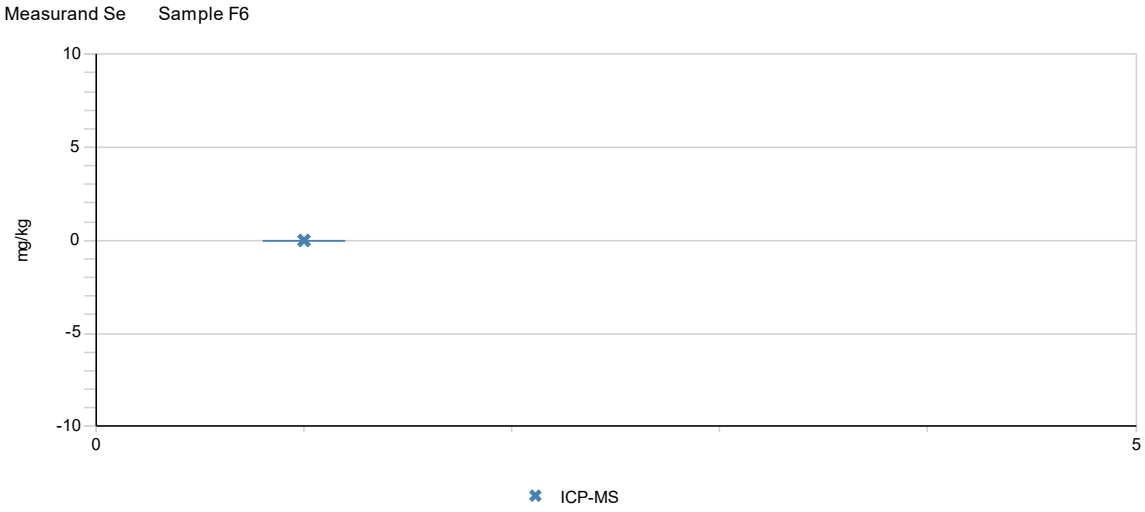

Measurand Se
Sample F1
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
mg/kg
0
5
ICP-MS

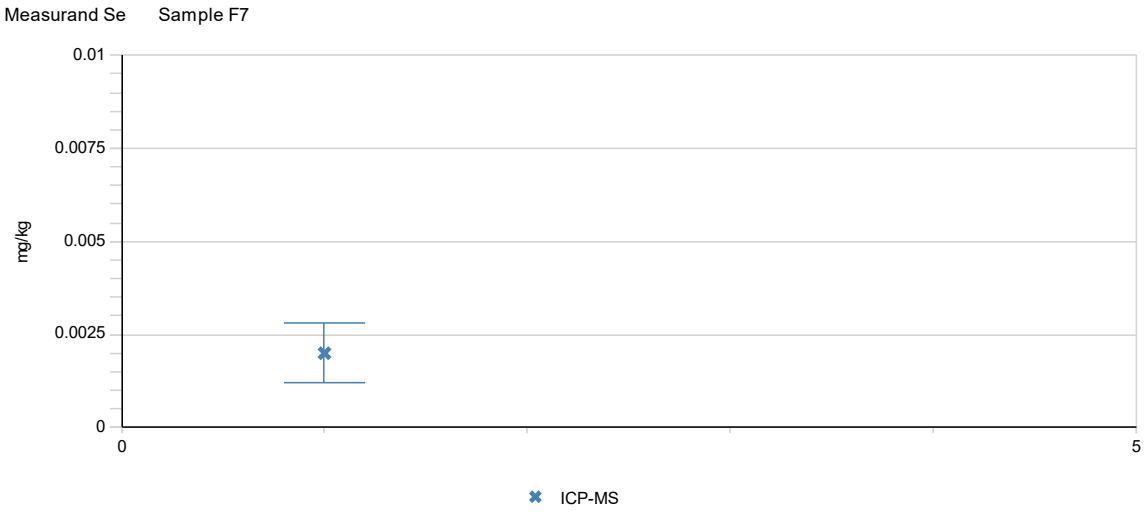

Measurand Se
Sample F2
0.04
0.035
0.03
0.025
0.02
0.015
0.01
mg/kg
0
5
ICP-MS

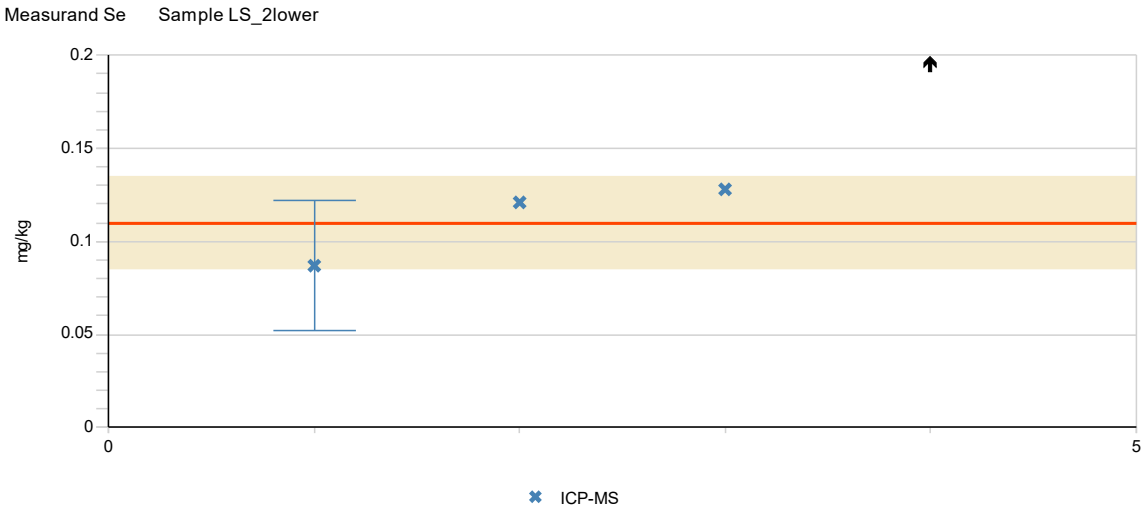

Measurand Se
Sample F3
0.06
0.05
0.04
0.03
0.02
0.01
mg/kg
0
5
ICP-MS

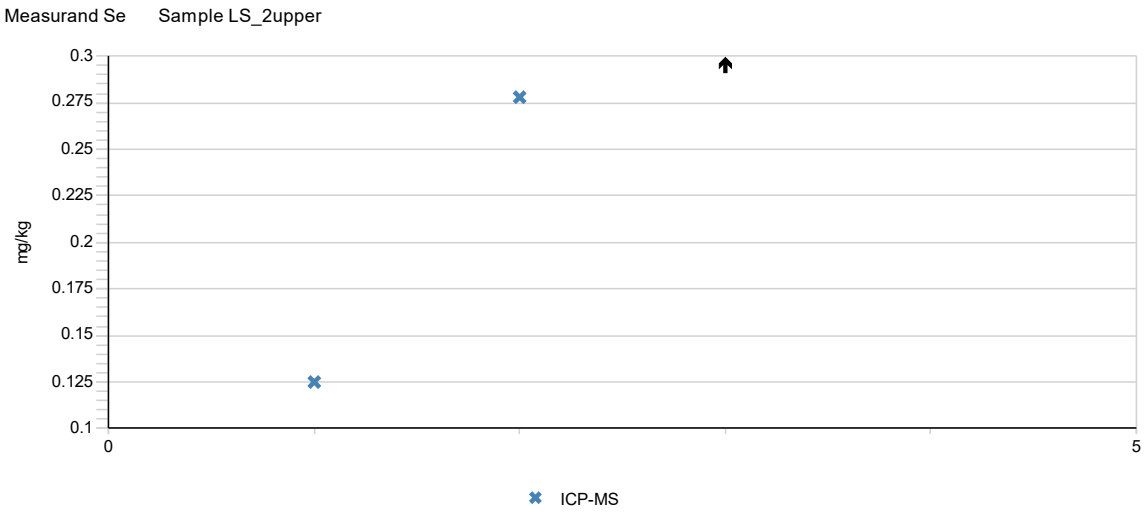

Measurand Se
Sample F4
0.015
0.013
0.011
0.009
0.007
0.005
0.003
0.001
mg/kg
0
5
ICP-MS


Measurand Se
Sample F5
0.001
0.0005
0
-0.0005
-0.001
mg/kg
0
5
ICP-MS

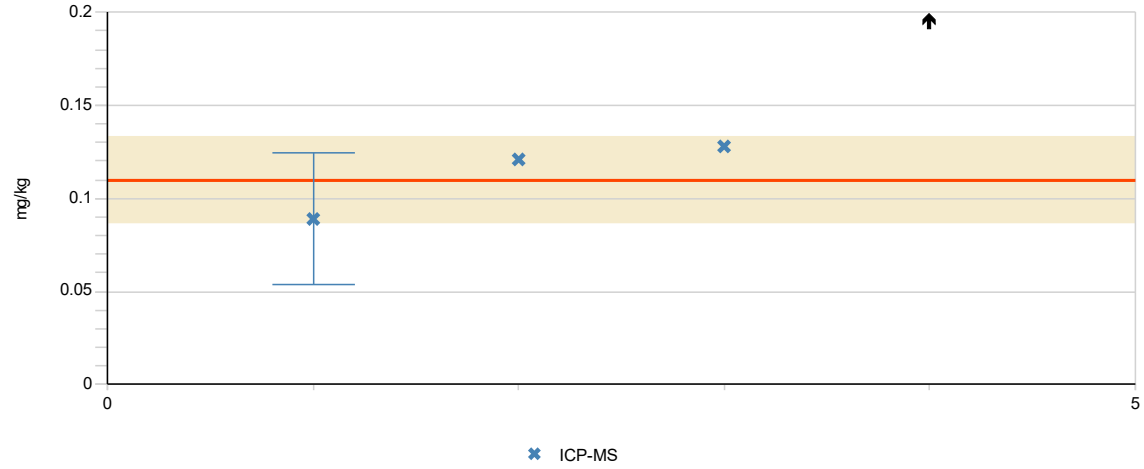

Measurand Se
Sample F6
10
5
0
-5
-10
mg/kg
0
5
ICP-MS


Measurand Se
Sample F7
0.01
0.0075
0.005
0.0025
0
mg/kg
0
5
ICP-MS

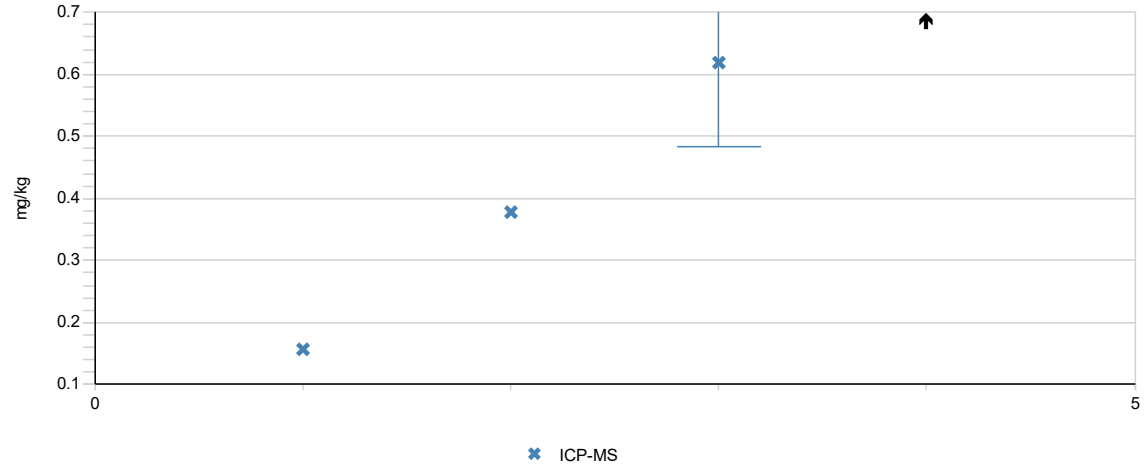

Measurand Se
Sample LS_2lower
0.2
0.15
0.1
0.05
0
mg/kg
0
5
ICP-MS


Measurand Se
Sample LS_2upper
0.3
0.275
0.25
0.225
0.2
0.175
0.15
0.125
0.1
mg/kg
0
5
ICP-MS

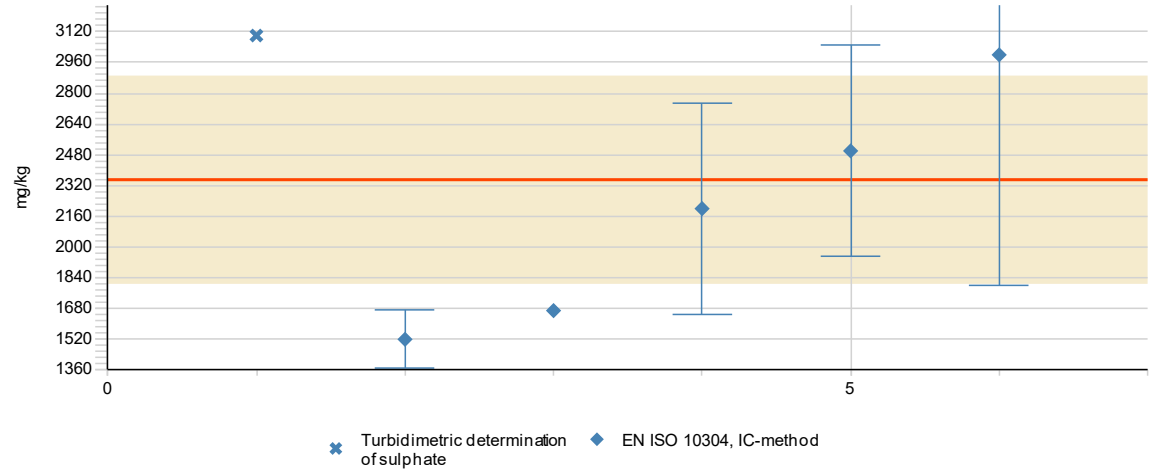
Measurand Se Sample LS10lower

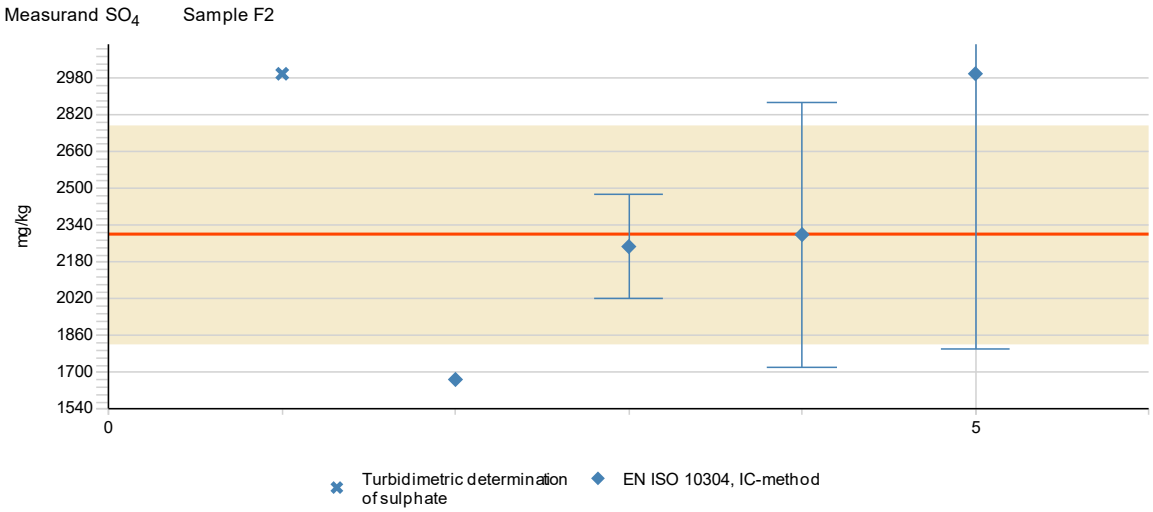


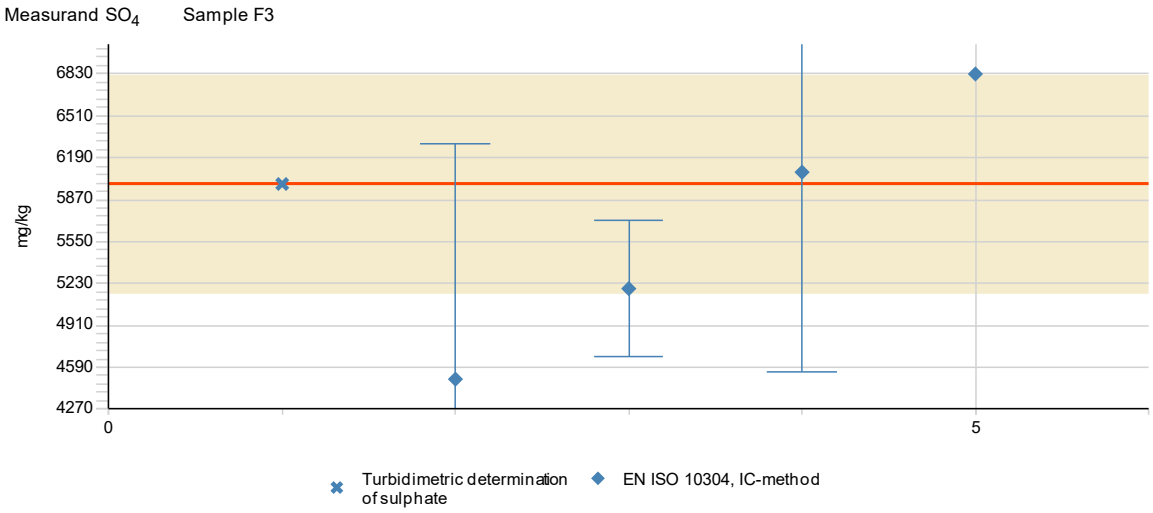

Measurand Se Sample LS10upper

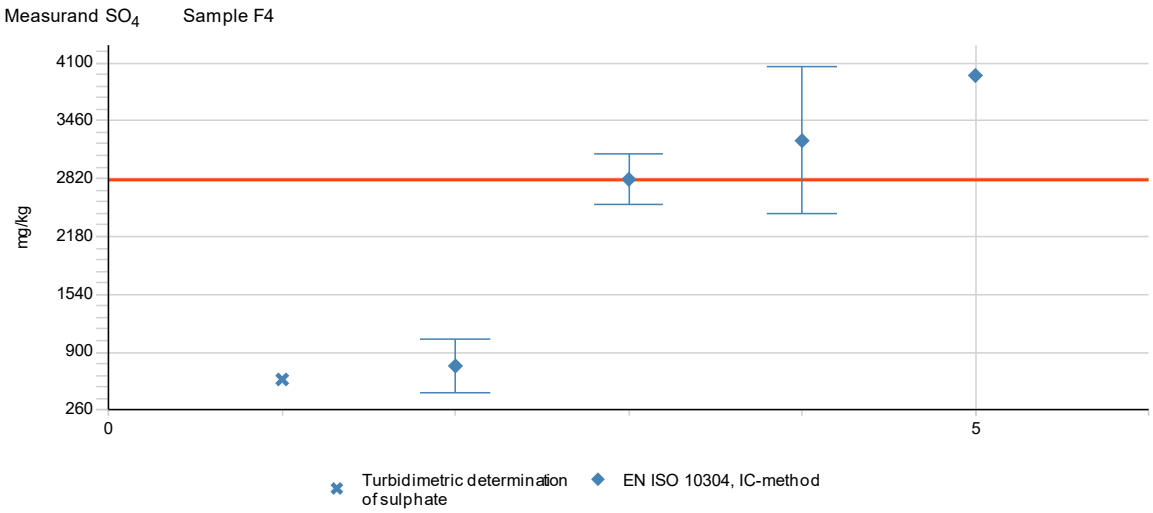



Measurand $SO_4$ Sample F1

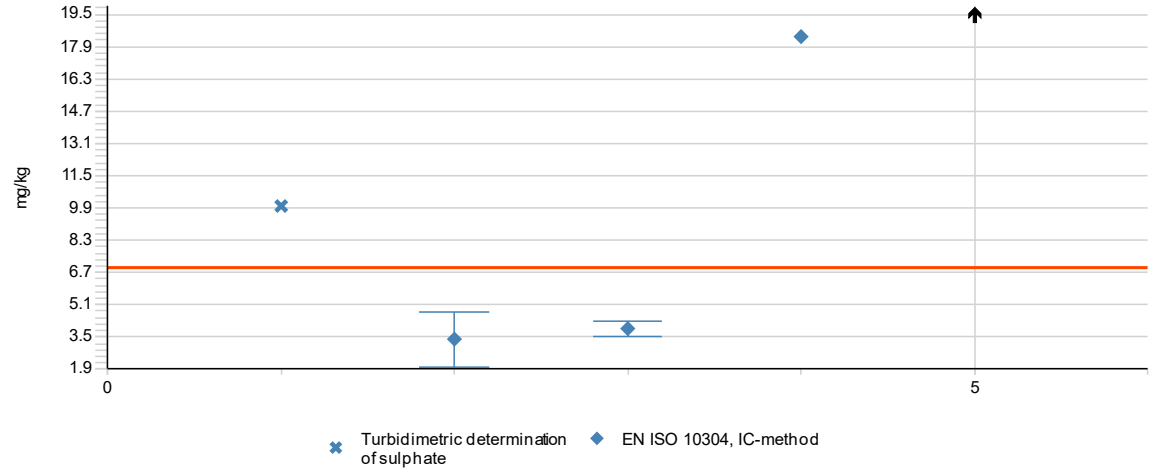



Measurand $SO_4$ Sample F2
mg/kg
2980
2820
2660
2500
2340
2180
2020
1860
1700
1540
0
5
Turbidimetric determination of sulphate
EN ISO 10304, IC-method

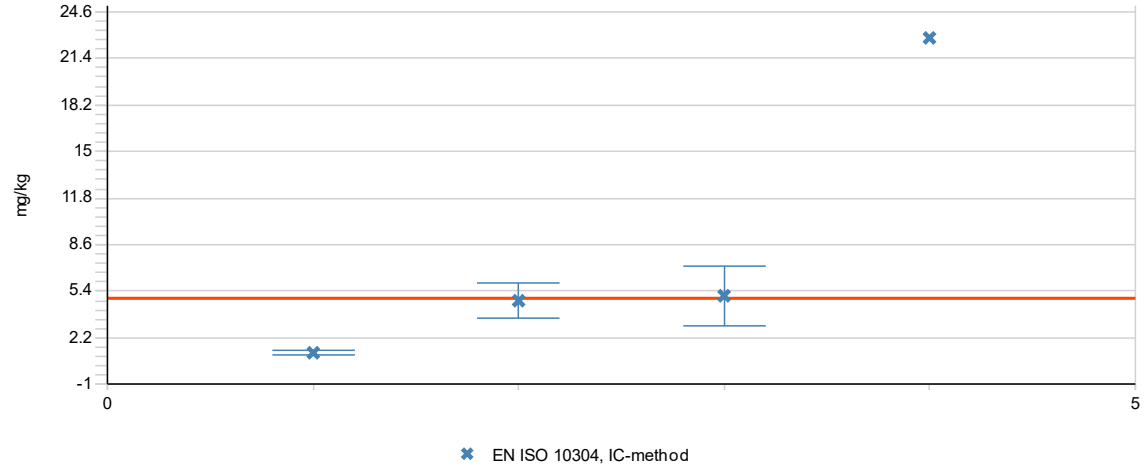

Measurand $SO_4$ Sample F3
mg/kg
6830
6510
6190
5870
5550
5230
4910
4590
4270
0
5
Turbidimetric determination of sulphate
EN ISO 10304, IC-method


Measurand $SO_4$ Sample F4
mg/kg
4100
3460
2820
2180
1540
900
260
0
5
Turbidimetric determination of sulphate
EN ISO 10304, IC-method

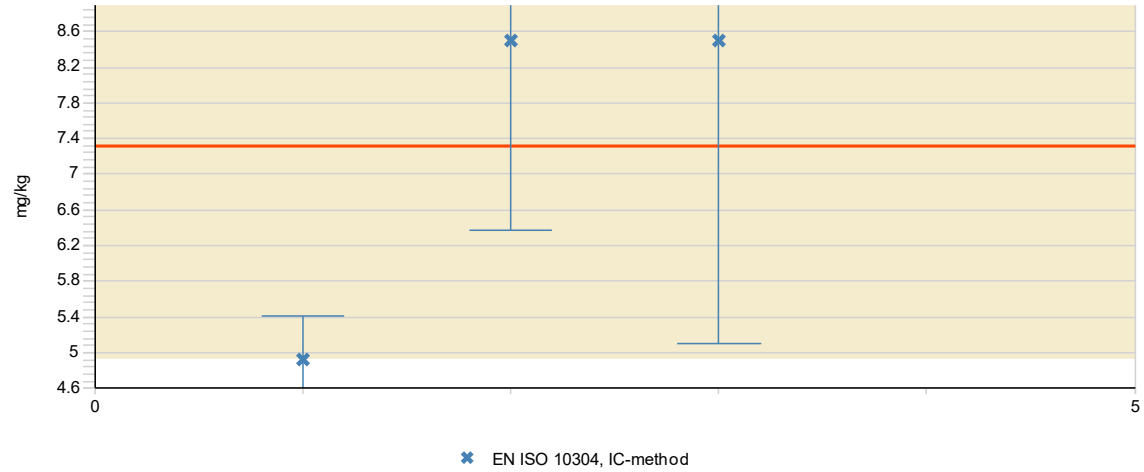
Measurand $SO_4$ Sample F5

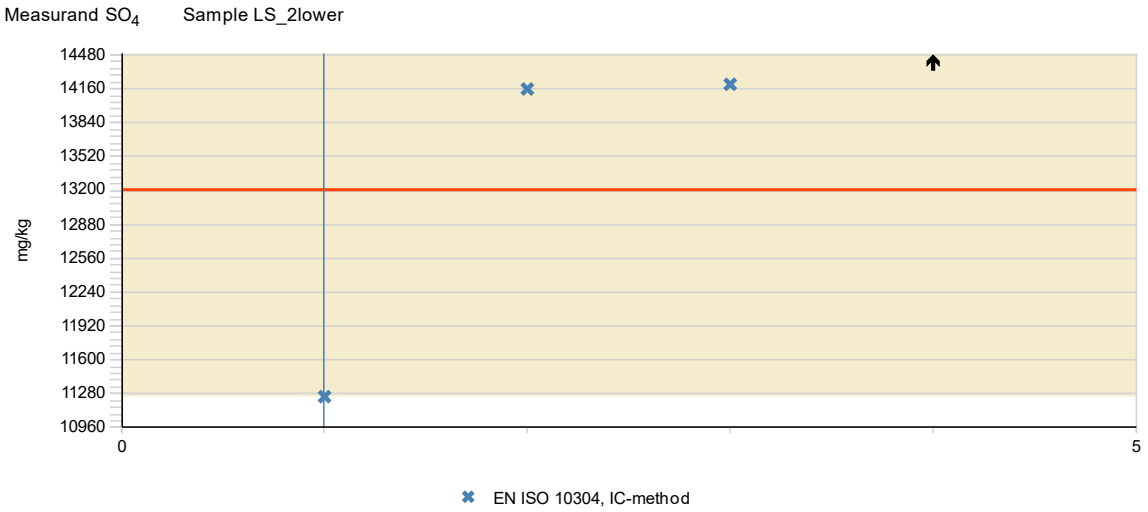


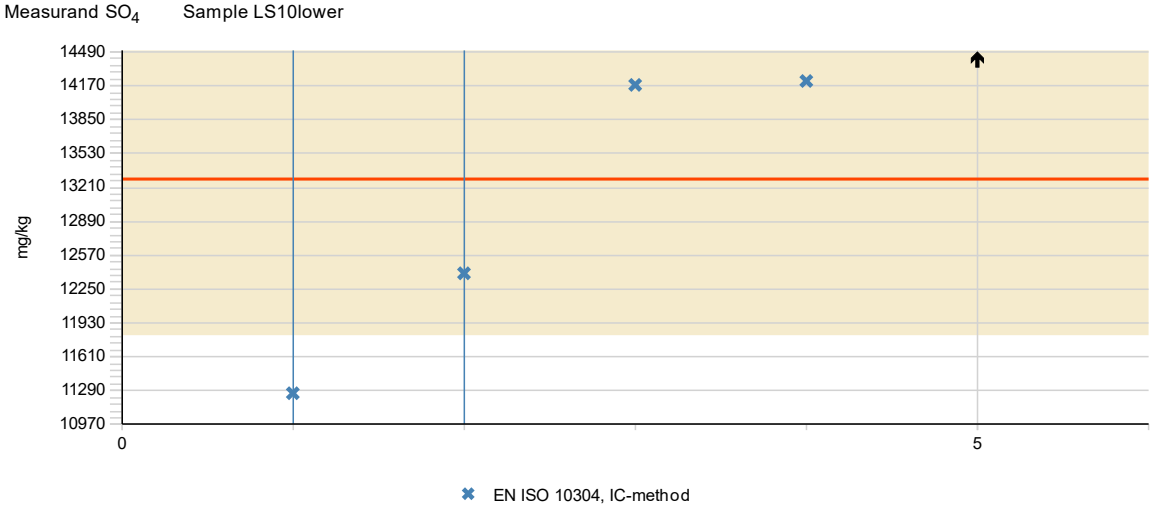

Measurand $SO_4$ Sample F6

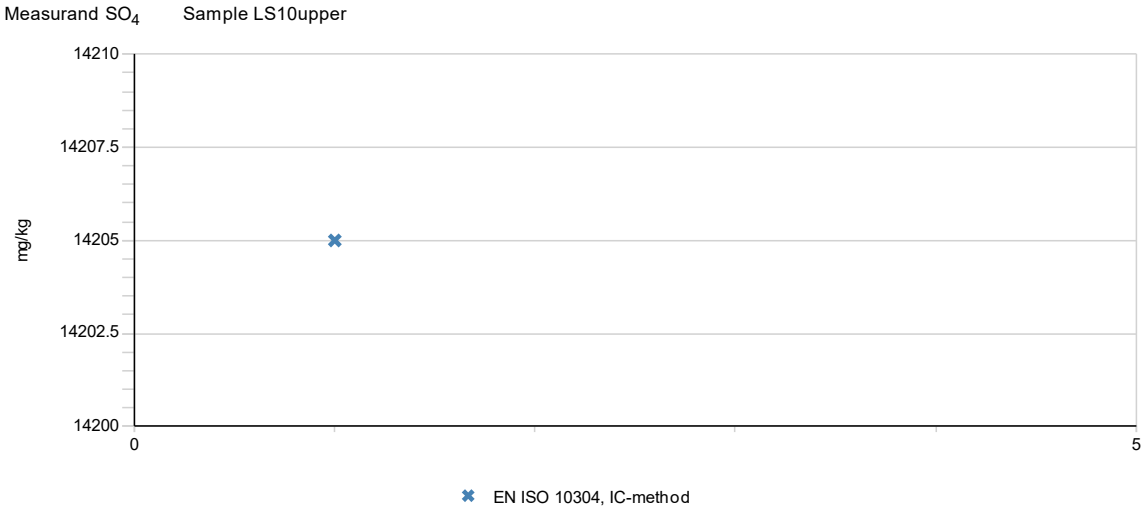


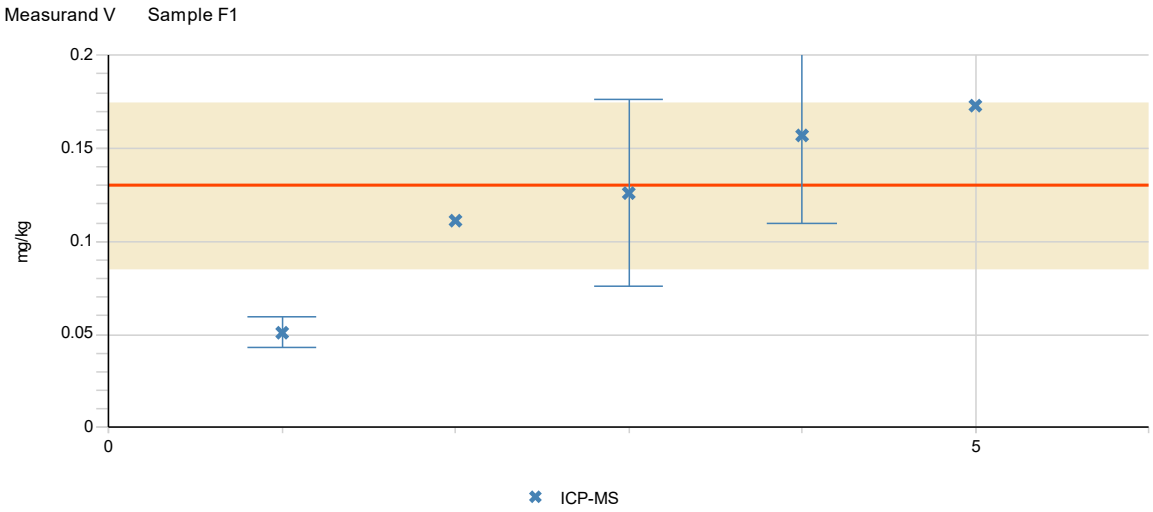

Measurand $SO_4$ Sample F7

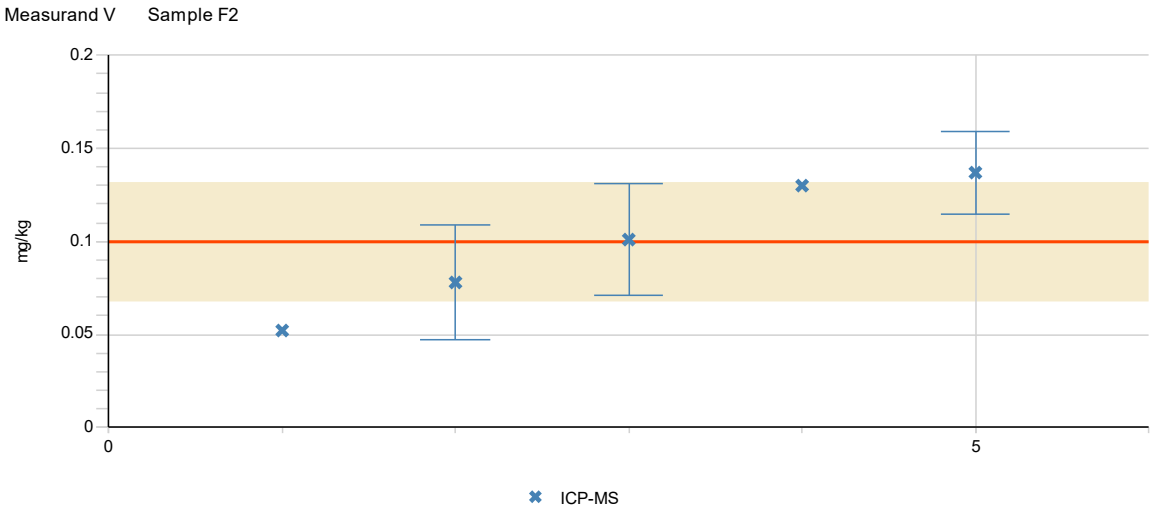


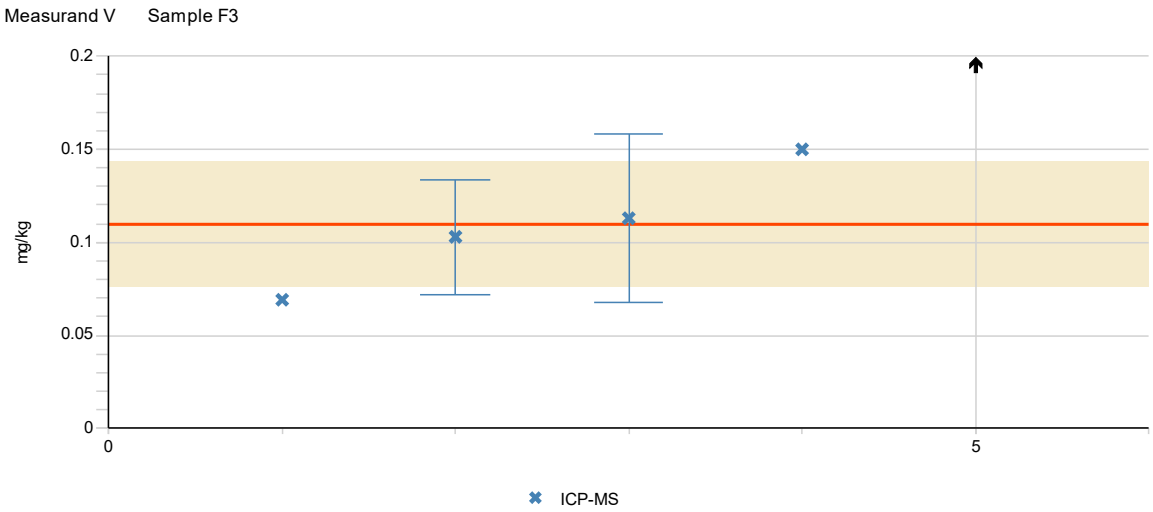

Measurand $SO_4$
Sample LS_2lower
14480
14160
13840
13520
13200
12880
12560
12240
11920
11600
11280
10960
mg/kg
0
5
EN ISO 10304, IC-method

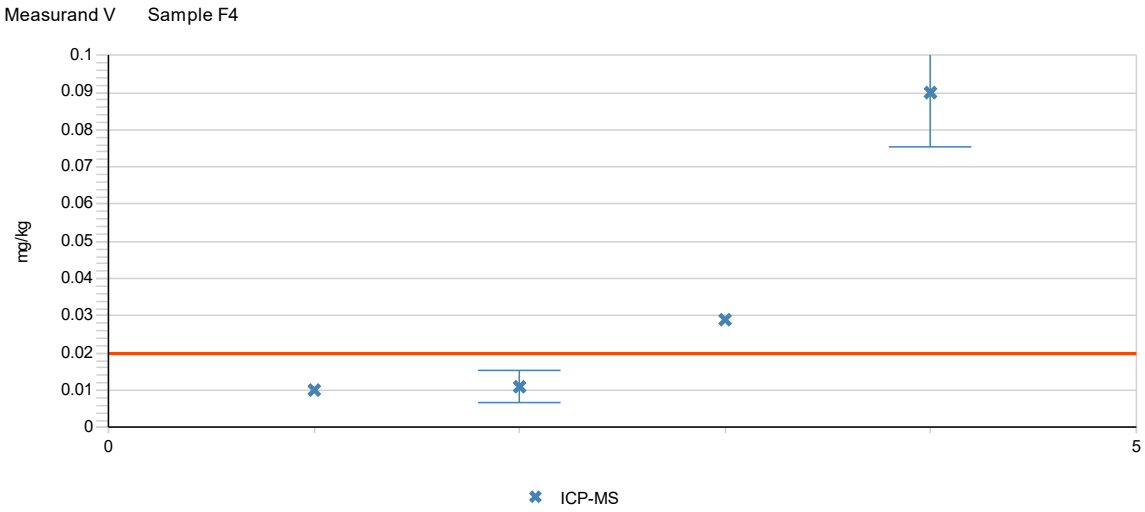

Measurand $SO_4$
Sample LS10lower
14490
14170
13850
13530
13210
12890
12570
12250
11930
11610
11290
10970
mg/kg
0
5
EN ISO 10304, IC-method

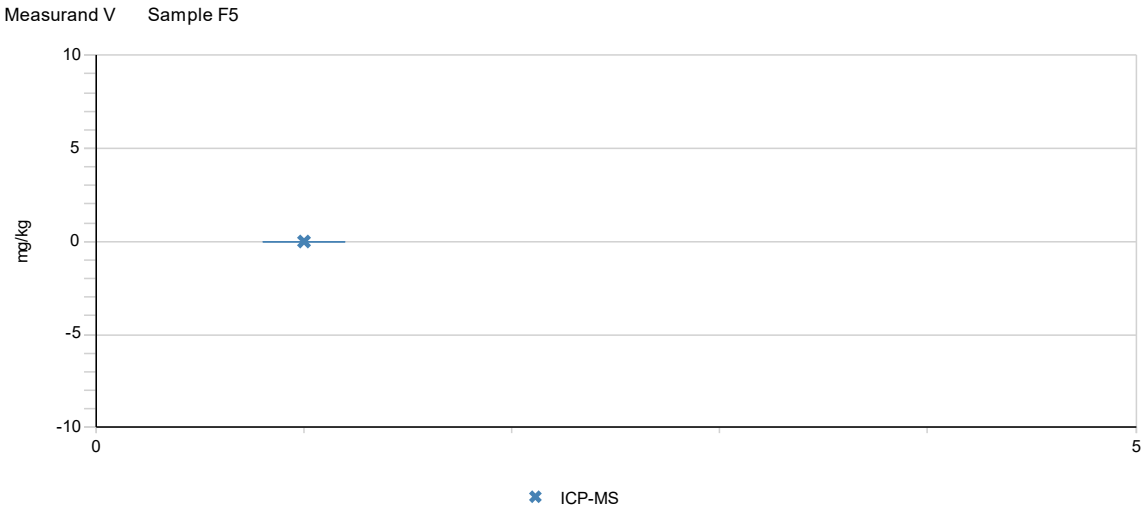

Measurand $SO_4$
Sample LS10upper
14210
14207.5
14205
14202.5
14200
mg/kg
0
5
EN ISO 10304, IC-method

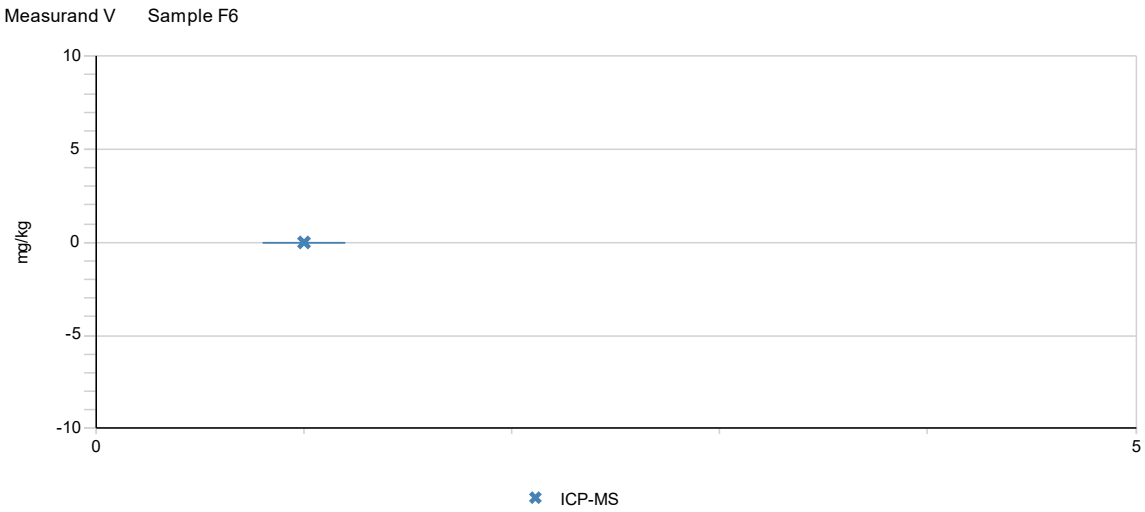

Measurand V Sample F1
0.2
0.15
0.1
0.05
0
mg/kg
0
5
ICP-MS


Measurand V Sample F2
0.2
0.15
0.1
0.05
0
mg/kg
0
5
ICP-MS

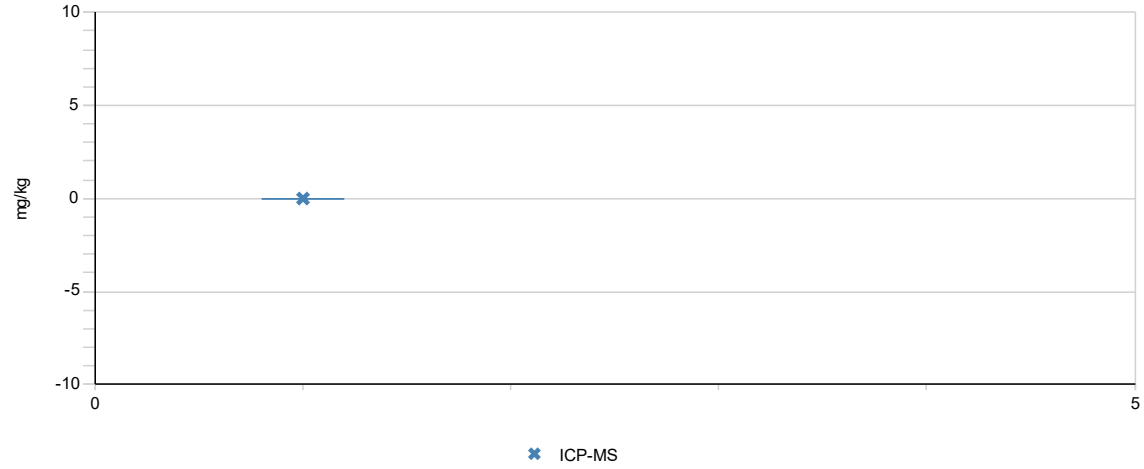

Measurand V Sample F3
0.2
0.15
0.1
0.05
0
mg/kg
0
5
ICP-MS


Measurand V Sample F4
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
mg/kg
0
5
ICP-MS

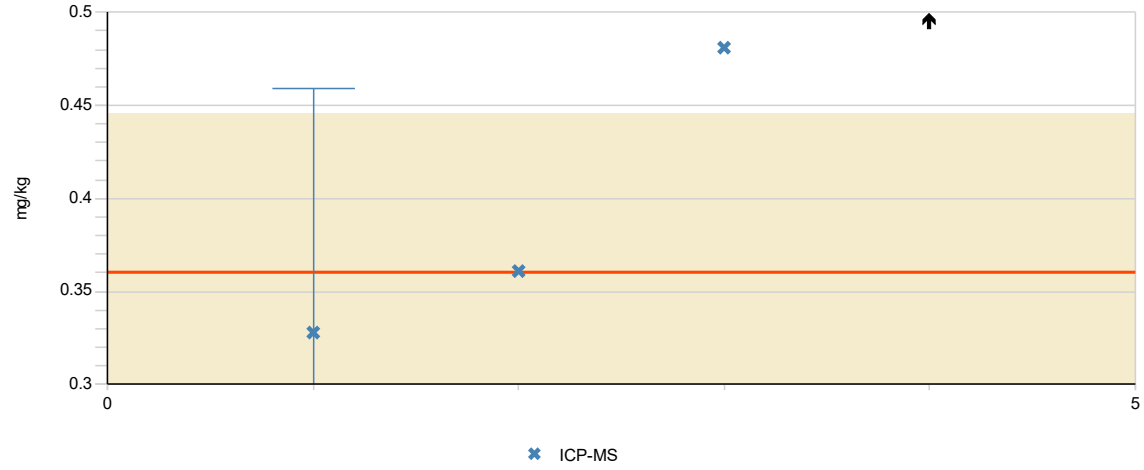

Measurand V Sample F5
10
5
0
-5
-10
mg/kg
0
5
ICP-MS


Measurand V Sample F6
10
5
0
-5
-10
mg/kg
0
5
ICP-MS

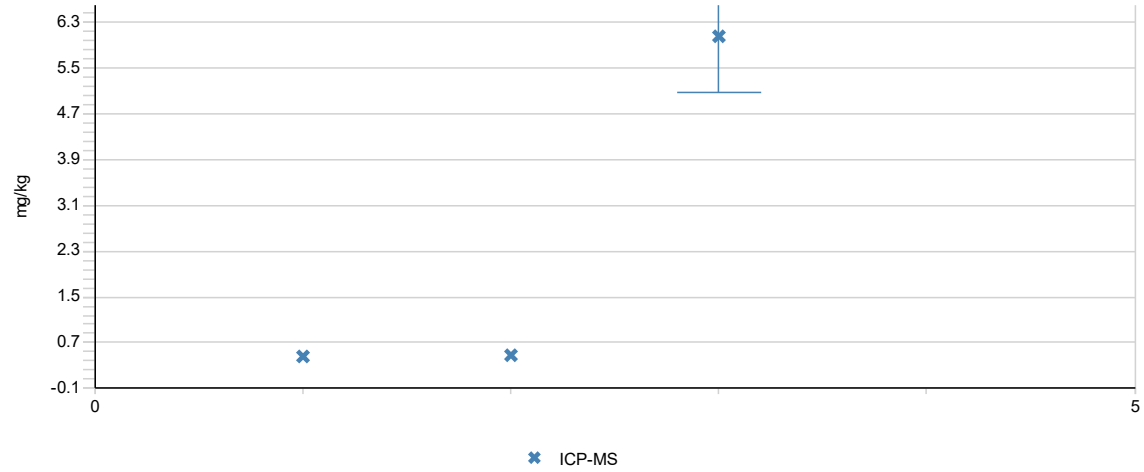
Measurand V Sample F7



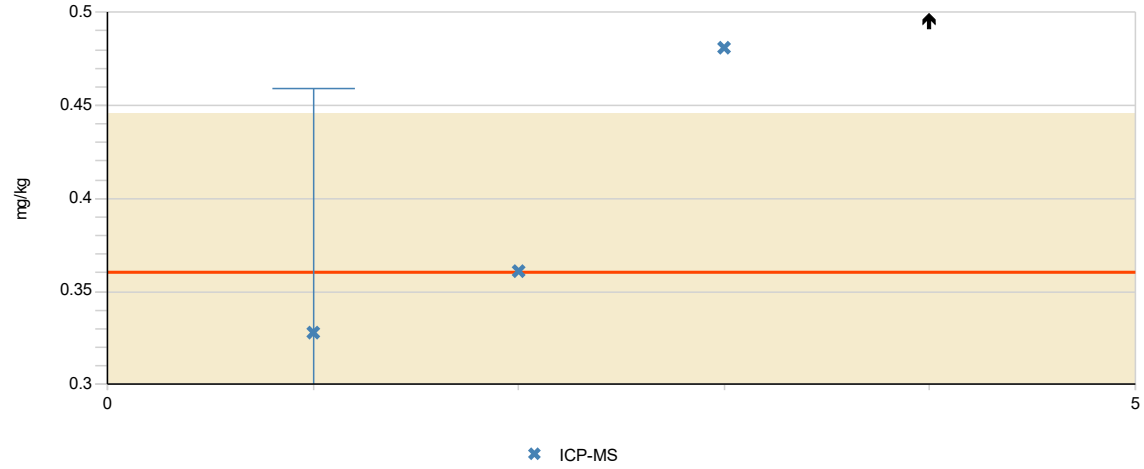

Measurand V Sample LS_2lower



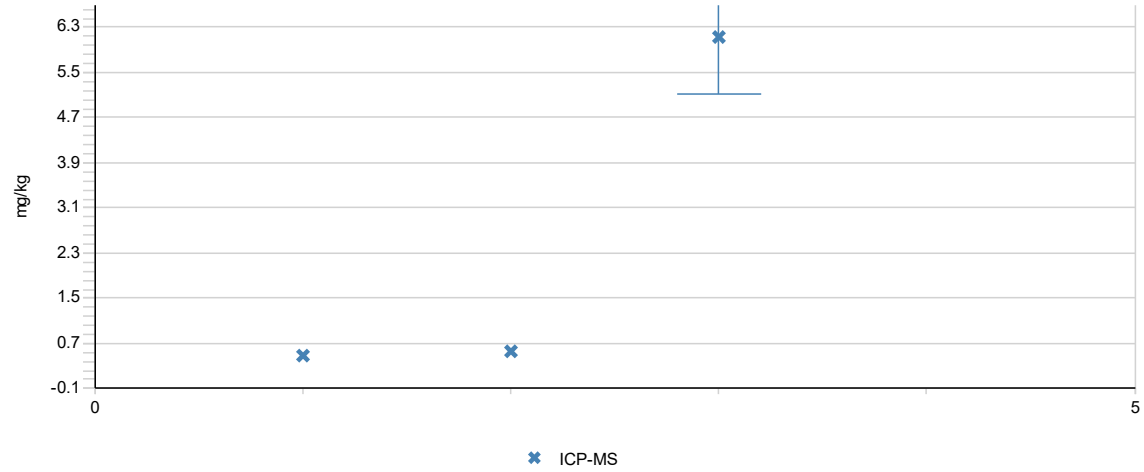

Measurand V Sample LS_2upper



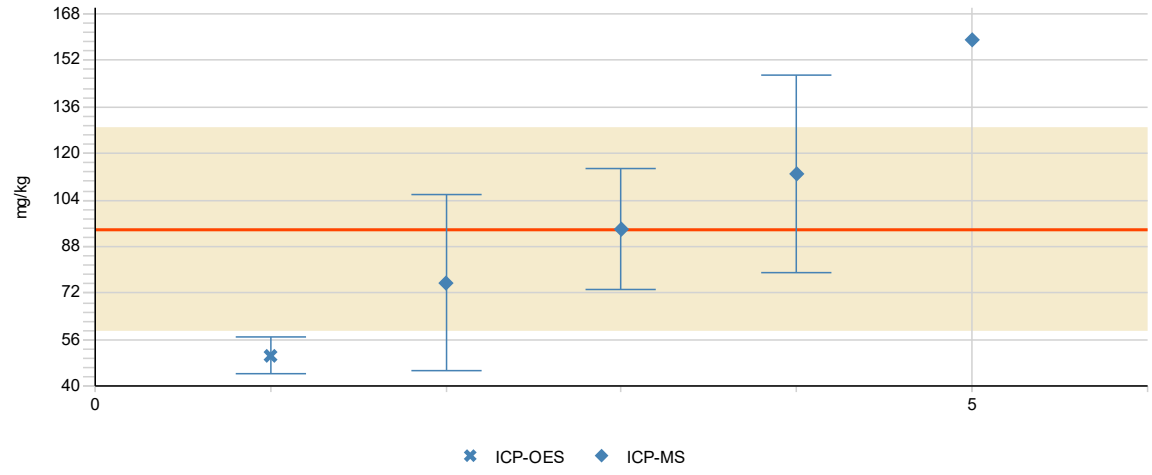
Measurand V Sample LS10lower



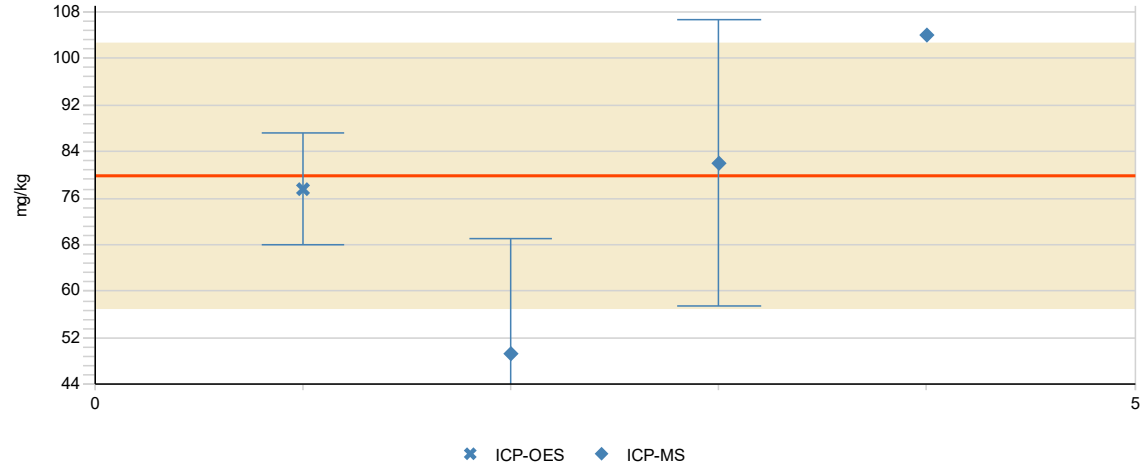

Measurand V Sample LS10upper



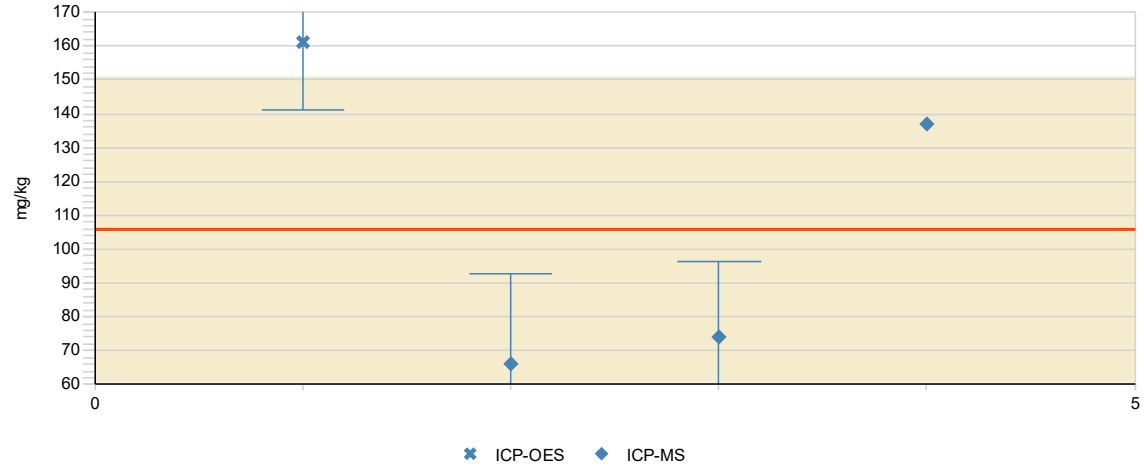

Measurand Zn Sample F1



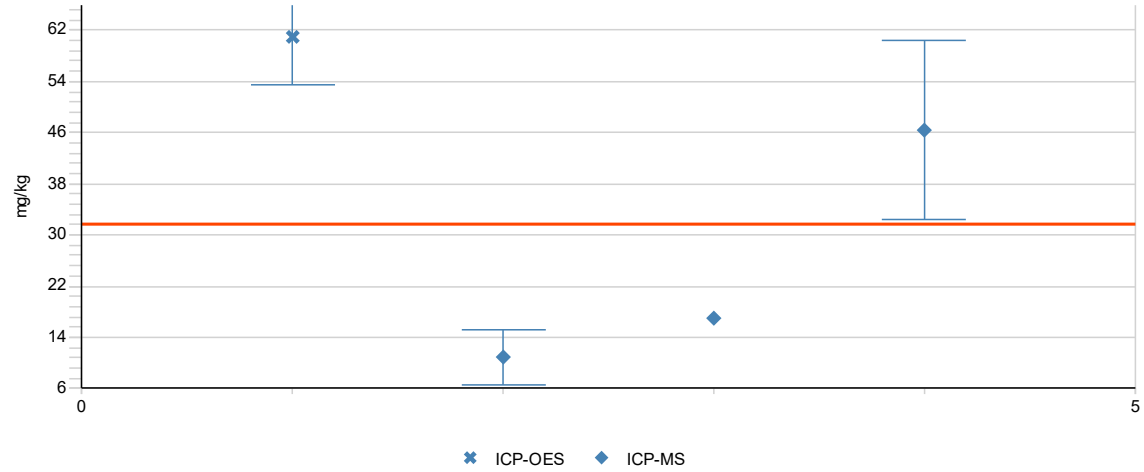
Measurand Zn Sample F2



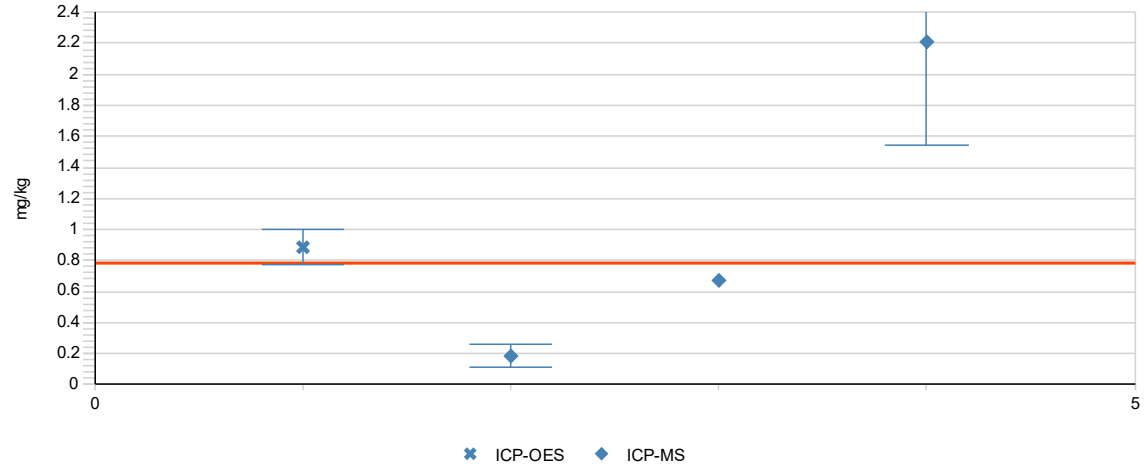

Measurand Zn Sample F3



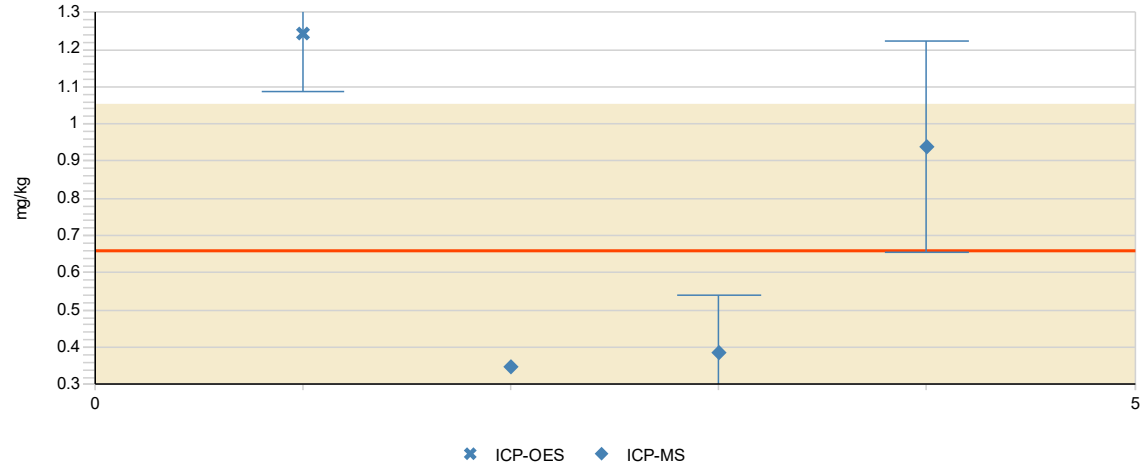

Measurand Zn Sample F4



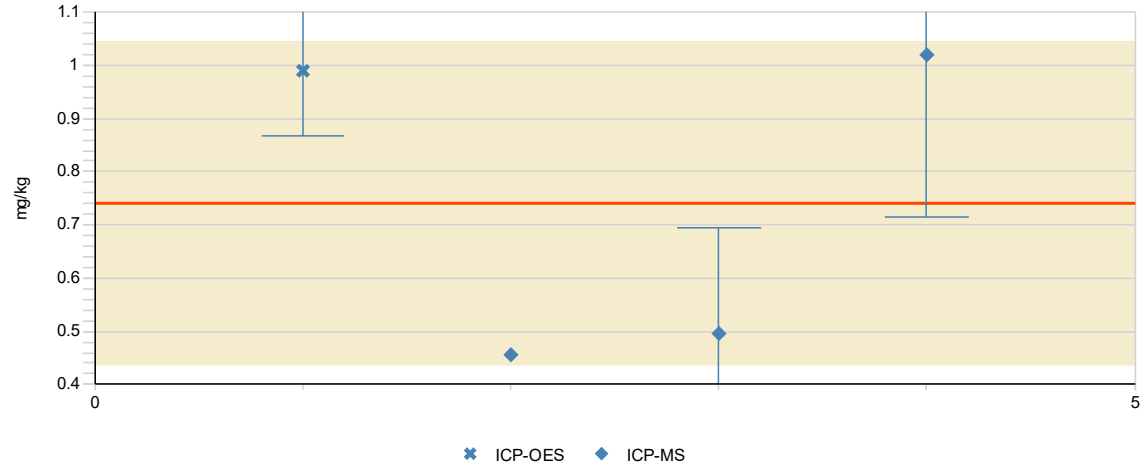
Measurand Zn Sample F5



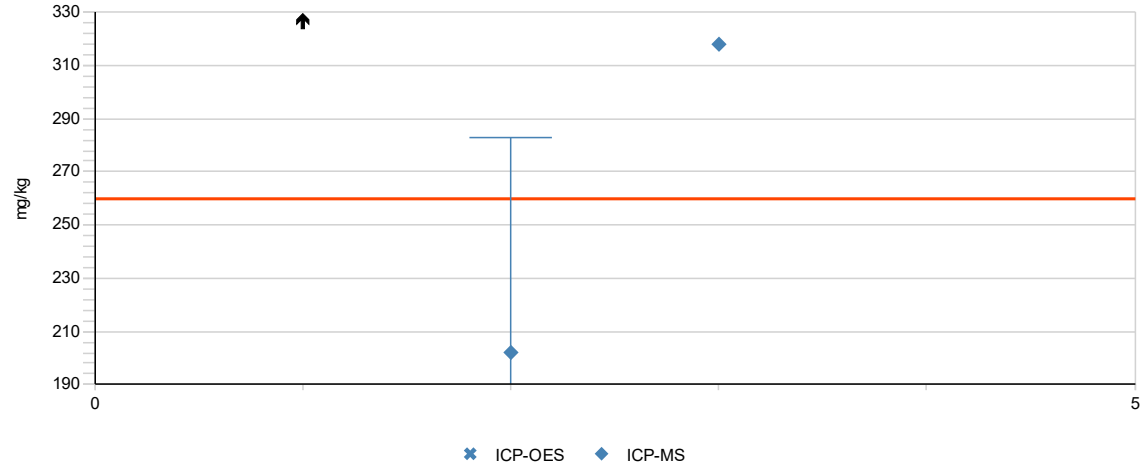

Measurand Zn Sample F6



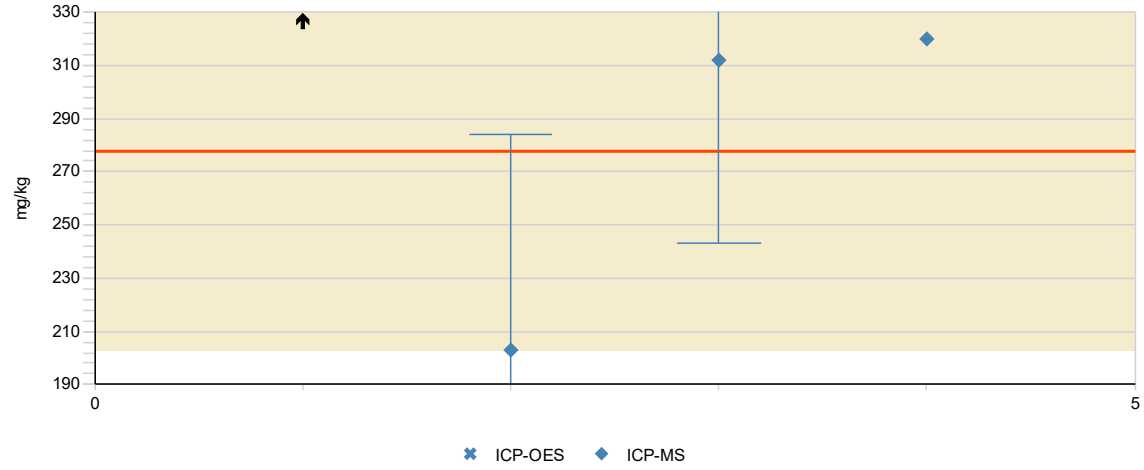

Measurand Zn Sample F7



Measurand Zn Sample LS_2lower

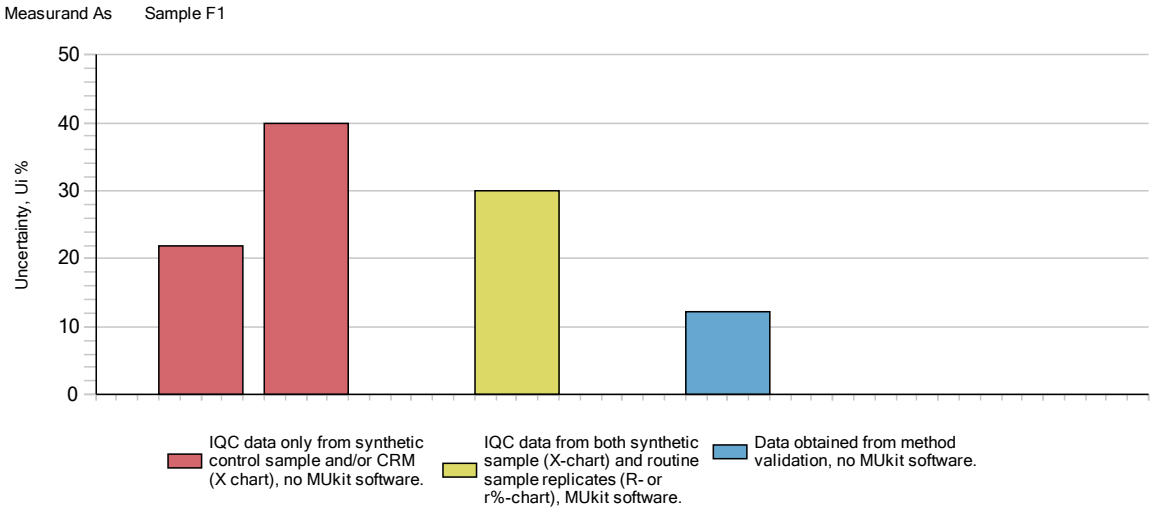


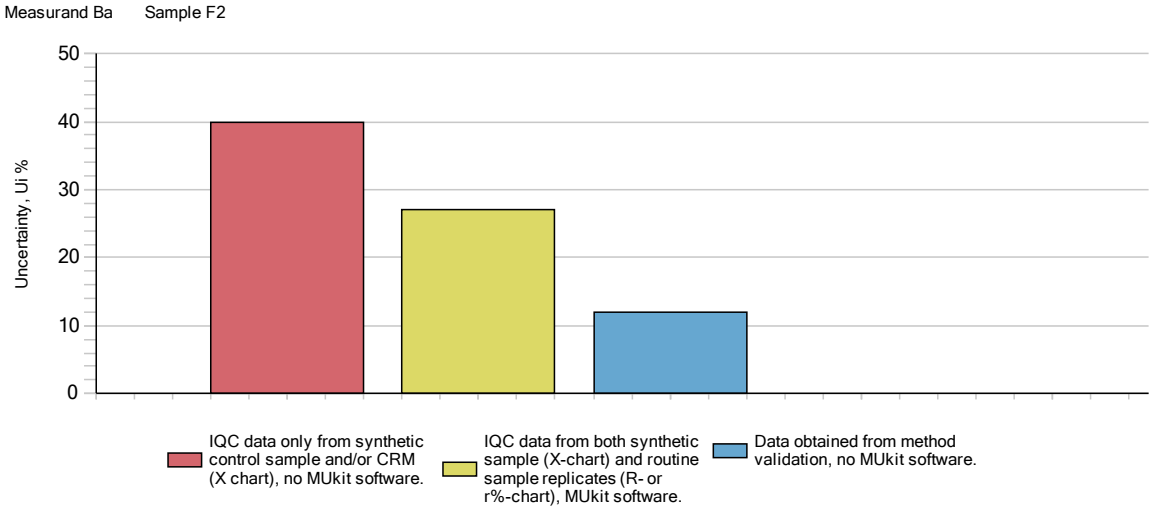

Measurand Zn Sample LS10lower



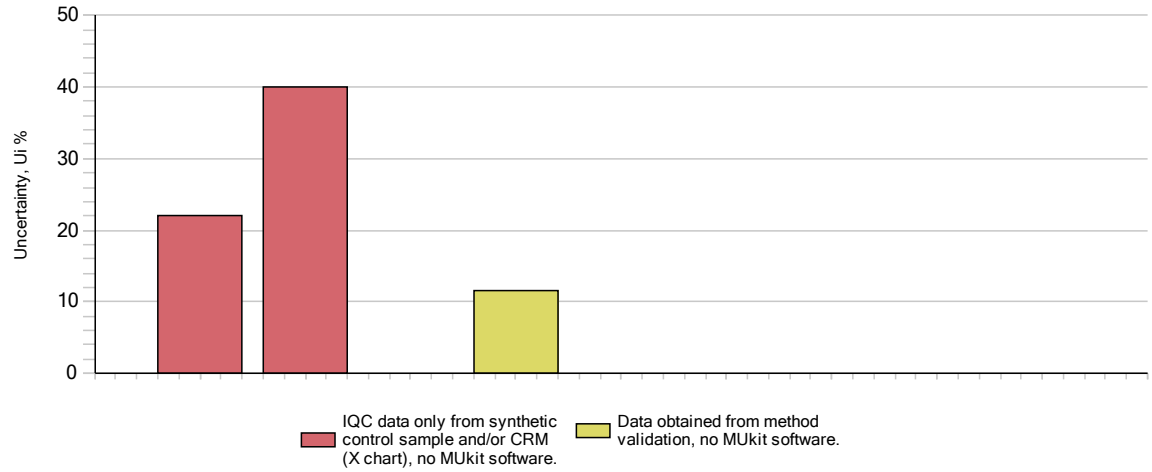
## Appendix 14. Examples of measurement uncertainties reported by the participants

In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level ($k$=2). The expanded uncertainties were estimated by using the internal quality control (IQC) data or data from method validation. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [8, 9].

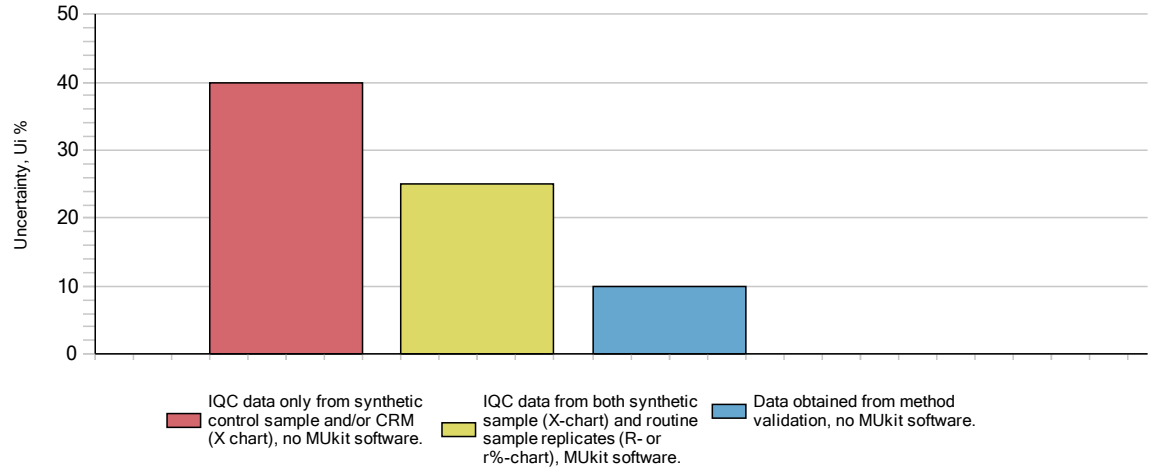


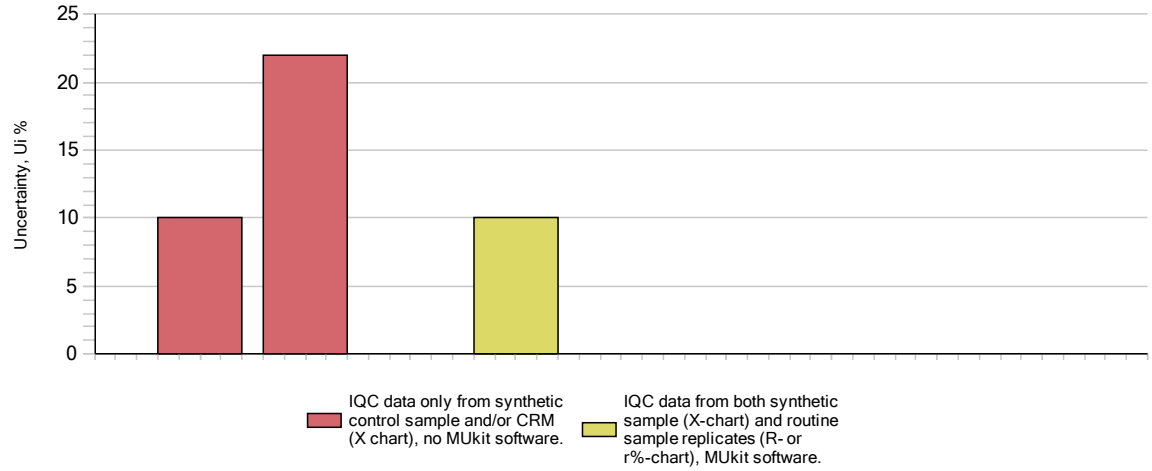
Measurand Cd Sample F1



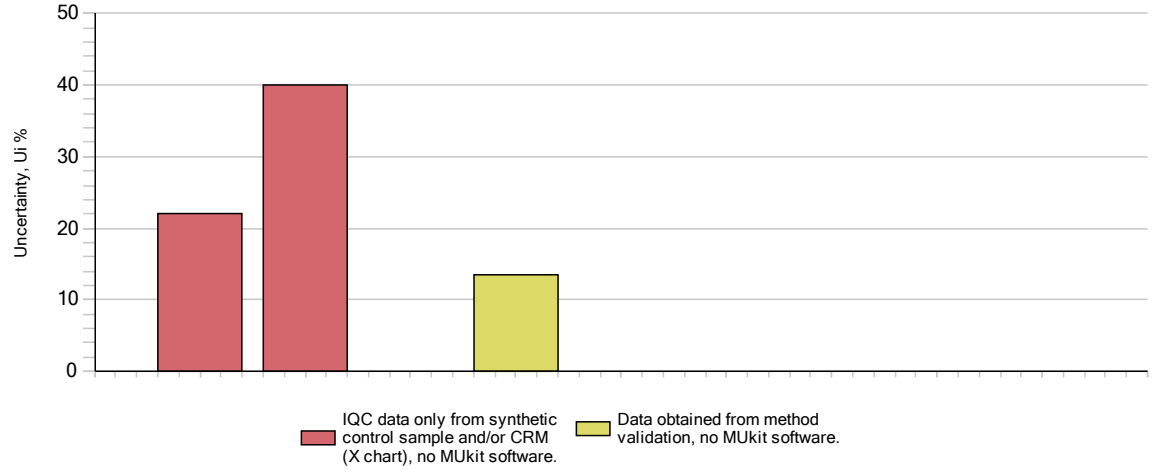

Measurand Cl Sample F5



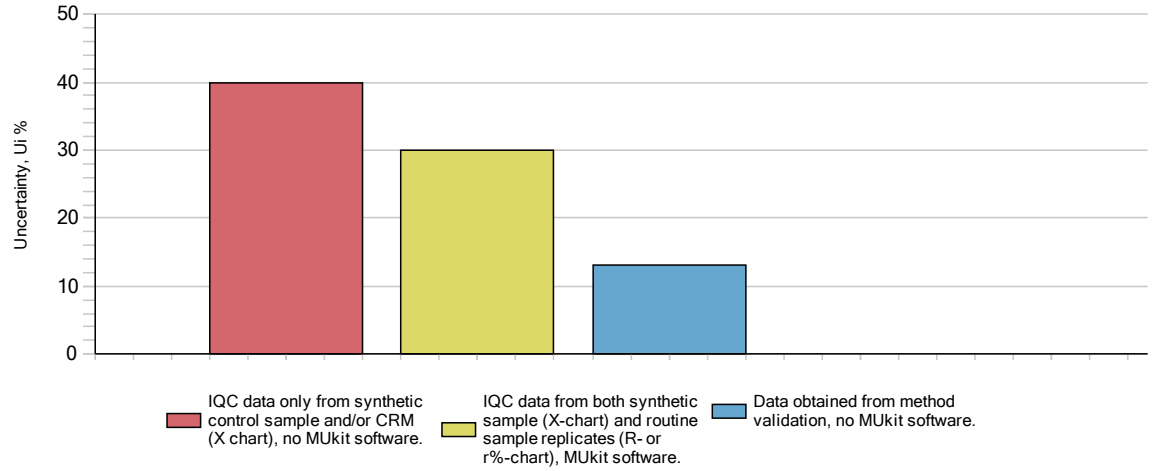

Measurand Conductivity Sample F7



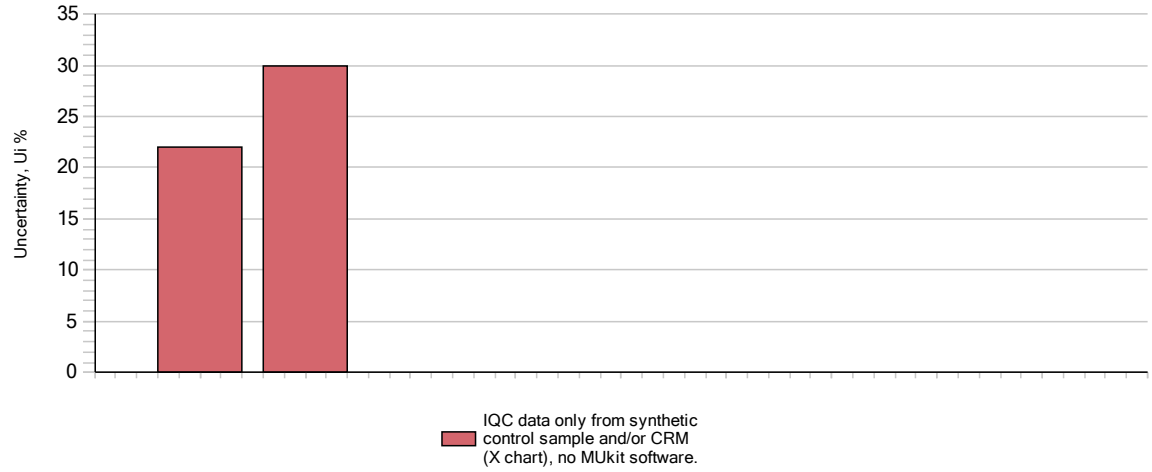
Measurand Cr Sample LS10lower



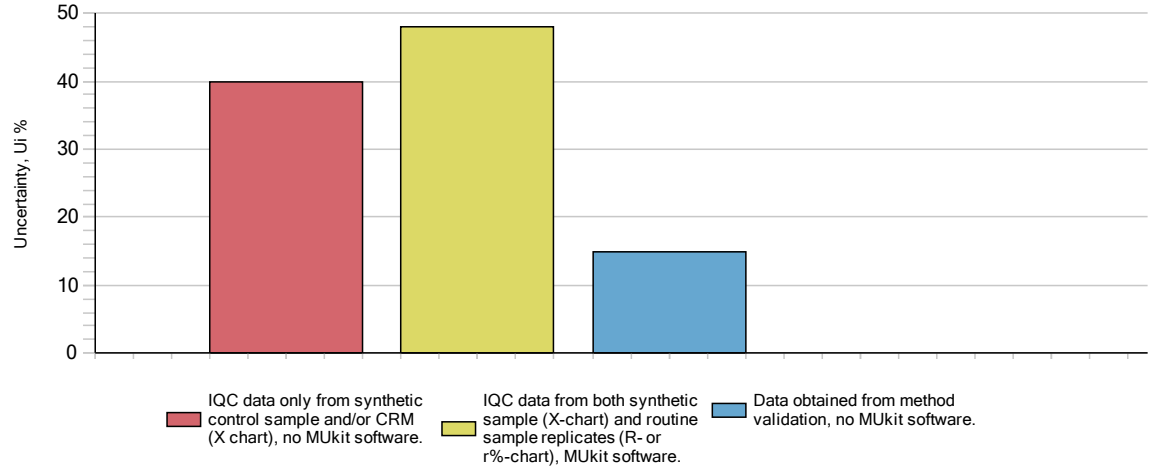

Measurand Cu Sample F3



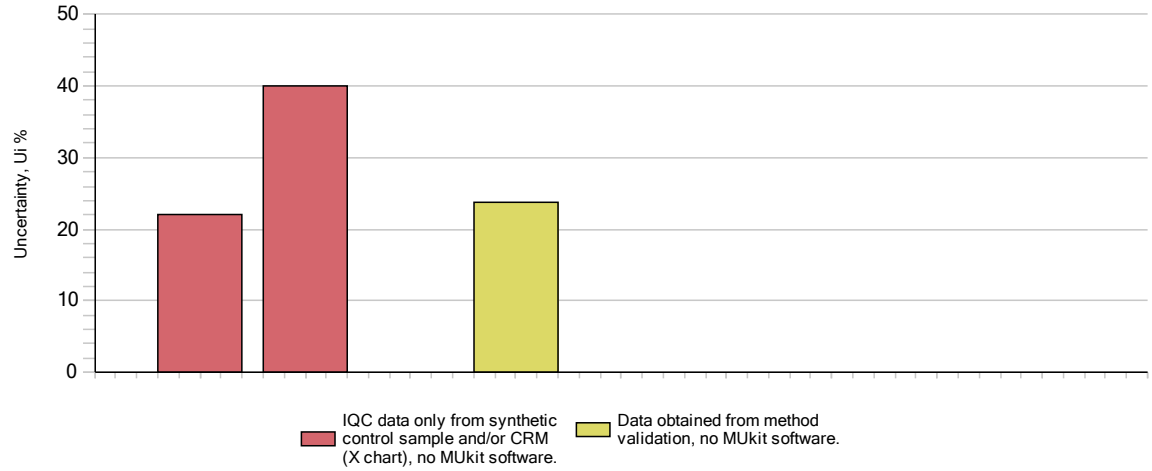

Measurand DOC Sample LS10lower



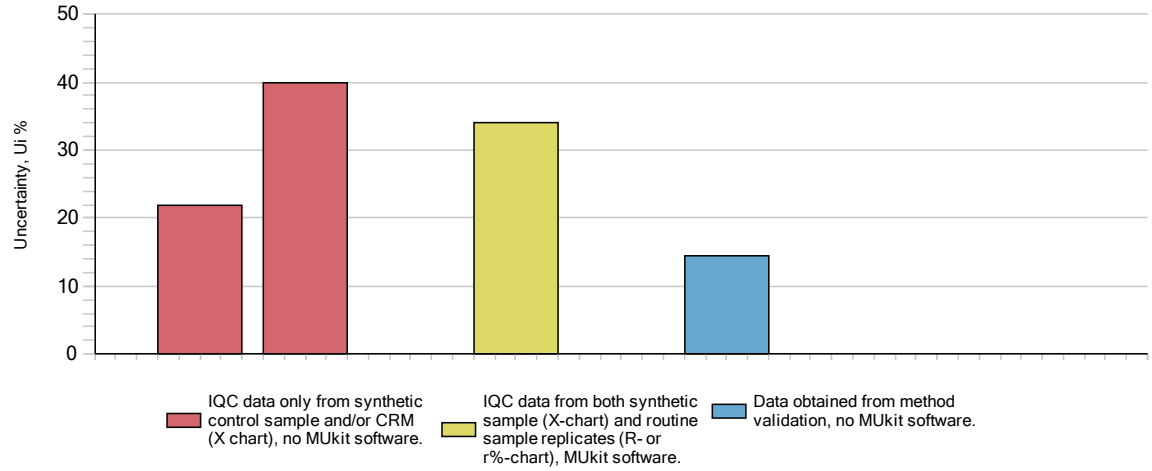
Measurand F Sample F4



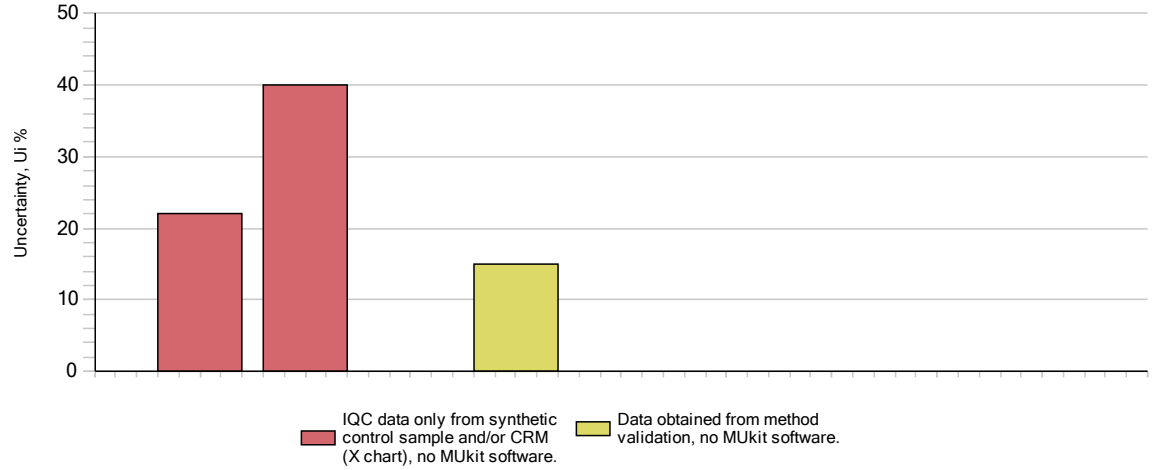

Measurand Hg Sample F1



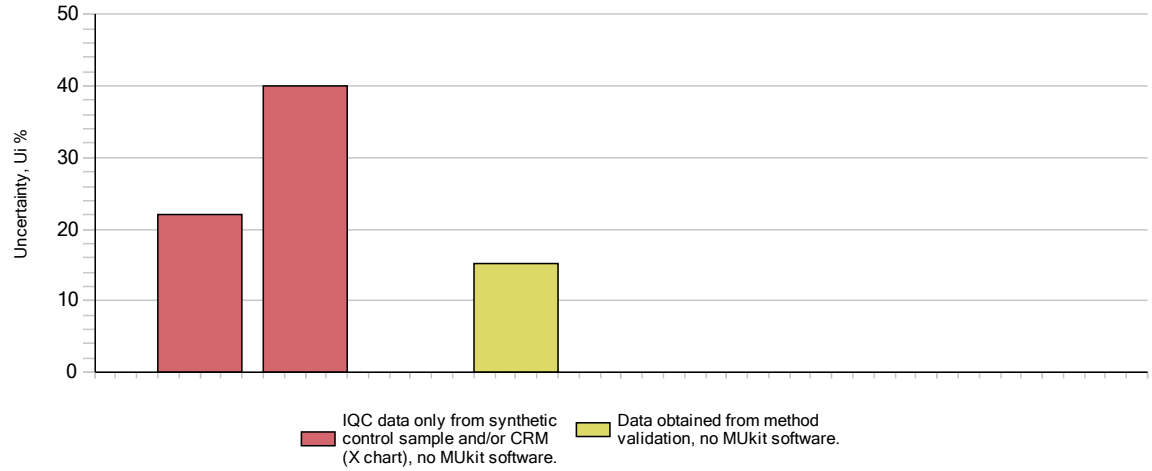

Measurand Mo Sample F1



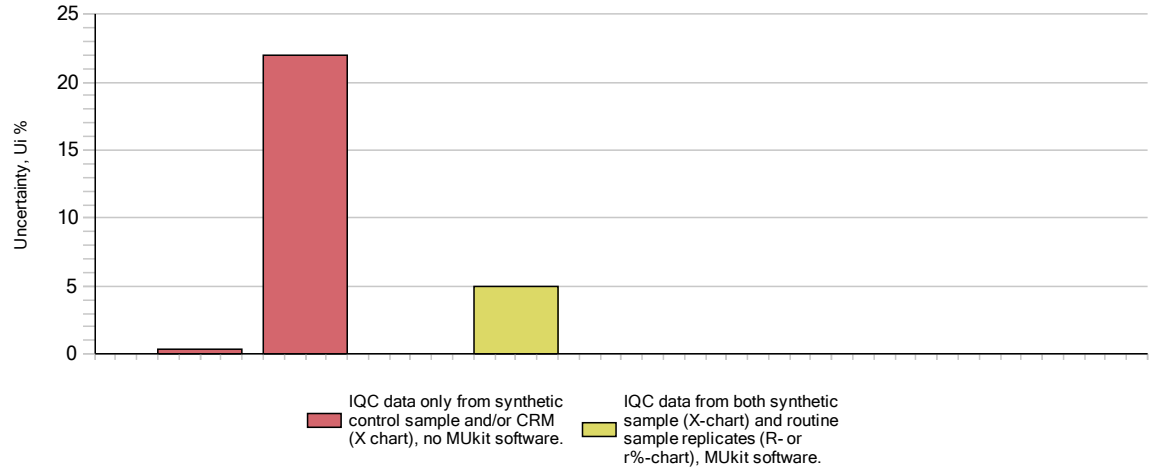
Measurand Ni Sample F1



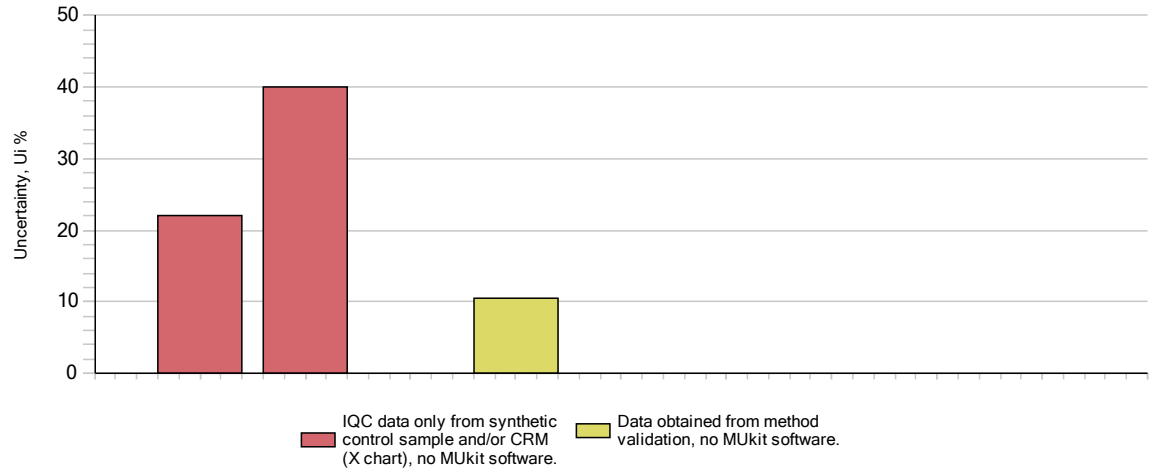

Measurand Pb Sample LS10lower



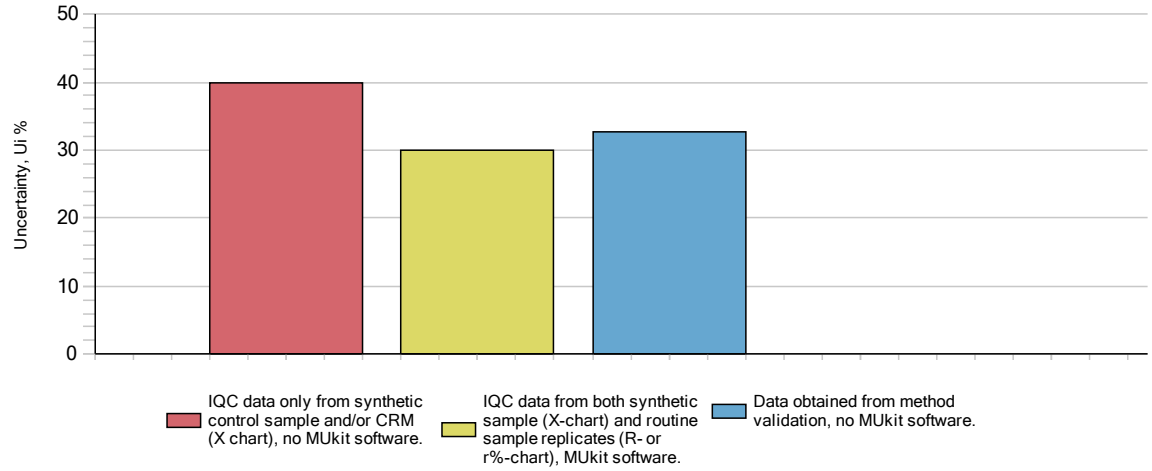

Measurand pH Sample F7



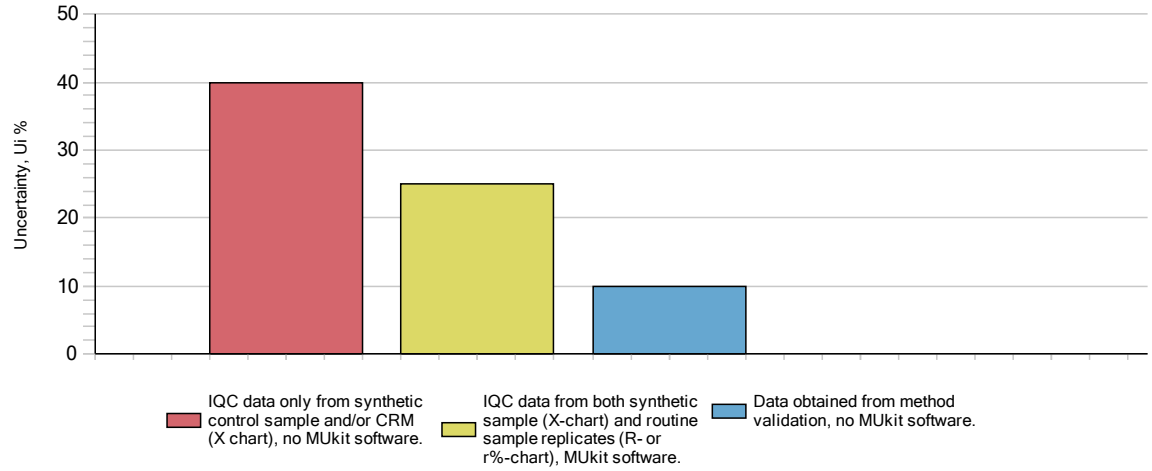
Measurand Sb Sample F1



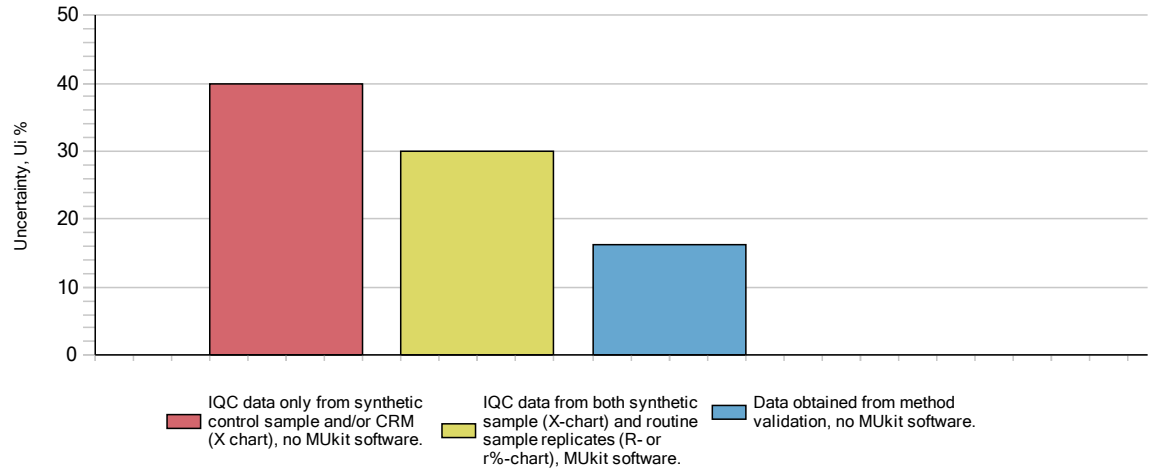

Measurand Se Sample F3



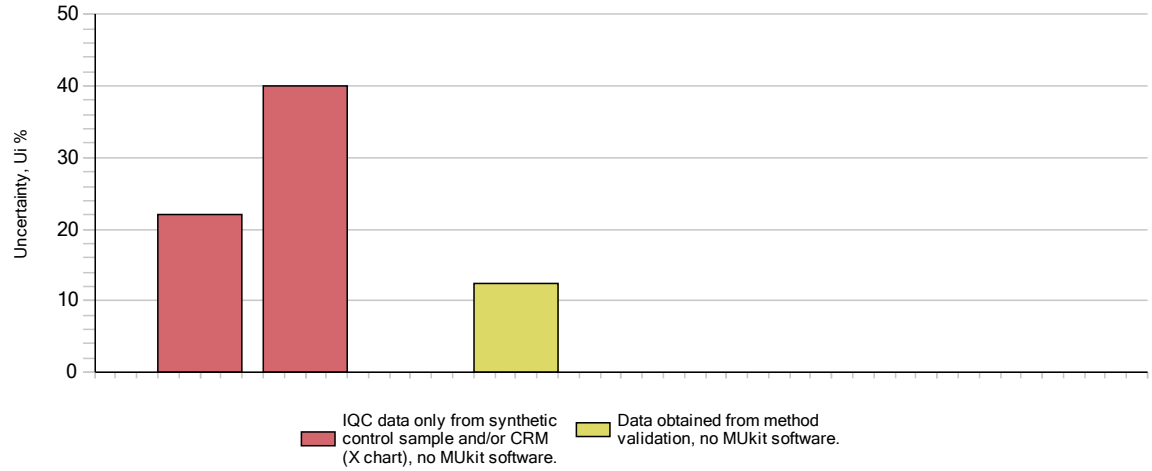

Measurand $SO_4$ Sample F2



Measurand V Sample F3




Measurand Zn Sample LS10lower



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